

Warm dust surface chemistry

H₂ and HD formation

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ABSTRACT

Context. Molecular hydrogen (H₂) is the main constituent of the gas in the planet-forming disks that surround many pre-main-sequence stars. H₂ can be incorporated in the atmosphere of the nascent giant planets in disks. Deuterium hydride (HD) has been detected in a few disks and can be considered the most reliable tracer of H₂, provided that its abundance throughout the disks with respect to H₂ is well understood.

Aims. We wish to form H₂ and HD efficiently for the varied conditions encountered in protoplanetary disks: the densities vary from 10⁴ to 10¹⁶ cm⁻³; the dust temperatures range from 5 to 1500 K, the gas temperatures go from 5 to a few 1000 Kelvin, and the ultraviolet field can be 10⁷ stronger than the standard interstellar field.

Methods. We implemented a comprehensive model of H₂ and HD formation on cold and warm grain surfaces and via hydrogenated polycyclic aromatic hydrocarbons in the physico-chemical code ProDiMo (PROtoplanetary DIsk MODEL). The H₂ and HD formation on dust grains can proceed via the Langmuir-Hinshelwood and Eley-Rideal mechanisms for physisorbed or chemisorbed H (D) atoms. H₂ and HD also form by H (D) abstraction from hydrogenated neutral and ionised PAHs and via gas phase reactions.

Results. H₂ and HD are formed efficiently on dust grain surfaces from 10 to ~ 700 K. All the deuterium is converted into HD in UV shielded regions as soon as H₂ is formed by gas-phase D abstraction reactions. The detailed model compares well with standard analytical prescriptions for H₂ (HD) formation. At low temperature, H₂ is formed from the encounter of two physisorbed atoms. HD molecules form on the grain surfaces and in the gas-phase. At temperatures greater than 20 K, the meeting between a weakly bound H- (or D-) atom or a gas-phase H (D) atom and a chemisorbed atom is the most efficient H₂ formation route. H₂ formation through hydrogenated PAHs alone is efficient above 80 K. However, the contribution of hydrogenated PAHs to the overall H₂ and HD formation is relatively low if chemisorption on silicate is taken into account and if a small hydrogen abstraction cross-section is used. The H₂ and HD warm grain surface network is a first step in the construction of a network of high-temperature surface reactions.

Key words. Astrochemistry; Molecular processes; Methods: numerical

1. Introduction

Molecular hydrogen is the most abundant molecule in virtually every interstellar environment from the Milky Way to high-redshift objects. Molecular mass estimates are uncertain because direct observations of H₂ are hampered by its homonuclear nature. In addition, the lowest pure-rotation transition of H₂ is not observable from the ground. H₂ is also important as one of the major coolants of the warm gas (Shull & Hollenbach 1978; Flower et al. 1986; Shaw et al. 2005; Hollenbach & Tielens 1999). In cold regions, the interactions of H₂ with cosmic rays initiate the efficient ion-neutral chemistry.

Protoplanetary disk masses derived from CO and isotopologue observations tend to give values that are lower than estimates from dust observations (Miotello et al. 2016; Thi et al. 2001). HD has been used to infer high gas masses in protoplanetary disks (Bergin et al. 2013; McClure et al. 2016). Detailed modeling of the H₂ and CO chemistry is required to determine protoplanetary disk masses.

H₂ is mostly formed on grain surfaces and thorough H-abstraction of hydrogenated polycyclic aromatic hydrocarbons (Wakelam et al. 2017; Gould & Salpeter 1963; Vidalí 2013) because the low density of most interstellar environments excludes H₂ formation by three-body reactions. When a hydrogen atom collides with the dust, it can weakly bound to the surface by the van der Waals forces (a few meV), the interaction is then of the physisorption type. It can also strongly bound to the surface by the covalent force (eV), and the interaction is called chemisorption. In cold molecular cloud conditions, the dust grains are mostly below 15 K, a temperature low enough for two weakly bound physisorbed hydrogen atoms to stay on the grain surfaces. The surface hydrogens scan the surfaces, meet each other, and recombine into H₂. In regions with dust temperatures higher than 20 K such as at the surface of photodissociation regions, only chemisorbed hydrogen atoms can remain on the grain surfaces. Hydrogen atoms can also chemically attach to polycyclic aromatic hydrocarbons (PAHs) to form hydrogenated PAHs or to amorphous carbon grains to form hydrogenated amorphous carbon. H₂ are subsequently formed by abstracting the hydrogen

from those species (Duley 1996; Pirronello et al. 1999; Mennella et al. 1999).

To account for the wide range of physical conditions (densities, gas and dust temperatures, radiation field) that occurs in planet-forming protoplanetary disks (Dutrey et al. 2014; Woitke et al. 2016), many physico-chemical disk models have implemented the H_2 formation model of Cazaux & Tielens (2002, 2004) through with an efficient H_2 formation on warm dust grains. The H_2 formation rate in the Interstellar medium (ISM) is constrained by precise observations obtained by the *Far Ultraviolet Spectroscopic Explorer* (FUSE) satellite at low density (Gry et al. 2002) and by the near-infrared H_2 emissions for dense Photodissociation Regions (PDRs) (Habart et al. 2004).

H_2 formation models mostly focus on specific environments. Detailed Monte-Carlo kinetic simulations have been used to model H_2 formation in the diffuse cloud environment (Chang et al. 2006; Iqbal et al. 2014; Iqbal et al. 2012). Hincelin et al. (2015) proposed a method to model H_2 formation on low temperature grain surfaces. Le Bourlot et al. (2012) implemented a detailed model of H_2 formation for photodissociation regions including Langmuir-Hinshelwood and Eley-Rideal mechanisms and Bron et al. (2014) studied H_2 formation on stochastically-heated small grains. Boschman et al. (2015) considered PAHs as an efficient medium for H_2 formation.

We present in this paper an H_2 formation model on warm dust grains and on hydrogenated PAHs. We have not considered H_2 formation on carbonaceous grains, which will be included in a future study. The model was designed to model H_2 formation for a large variety of physical conditions as found in protoplanetary disks. The results are compared to the formation rates computed using semi-analytical H_2 formation formulations. Our model relies on a set of measured and theoretical data.

Experimental studies on H_2 formation have been performed on cold ($T_d < 20$ K) polycrystalline (Pirronello et al. 1997) and amorphous silicates (Katz et al. 1999; Perets et al. 2007; Vidali et al. 2007; He et al. 2011; Gavilan et al. 2012). Physisorption of atomic hydrogen proceeds without a barrier (Downing et al. 2013; Navarro-Ruiz et al. 2014). He et al. (2011) concluded that the desorption energy distribution of the newly-formed HD is much broader if HD forms on an amorphous rather than on a crystalline silicate surface.

Other studies concentrate on the H_2 formation (Perets et al. 2005; Roser et al. 2002; Manicò et al. 2001) on amorphous water ice since water ice mantles cover most grains at $A_V \gtrsim 3$ mag (Boogert et al. 2015).

Once on a grain surface, an atomic hydrogen can diffuse and meet another atom. H atom diffusion on amorphous ice has been studied experimentally (Matar et al. 2008; Masuda et al. 1998; Watanabe et al. 2010; Hama et al. 2012; Dupuy et al. 2016) and theoretically (Al-Halabi & van Dishoeck 2007; Veeraghattam et al. 2014). The encounter between two atoms results in the H_2 formation. This reaction occurs with no or a small activation barrier of ~ 250 K (Navarro-Ruiz et al. 2014). This mechanism, which involves two adsorbed species, is called the Langmuir-Hinshelwood mechanism (Hama & Watanabe 2013). An adsorbed H-atom can also react with an impinging gas-phase H atom to form H_2 in the so-called Eley-Rideal process.

At dust temperatures above ~ 20 K, the surface residence time of physisorbed H atoms is so low that H_2 is not produced efficiently anymore. Only chemisorbed atoms remain on the surfaces long enough for H_2 to form. The formation of chemisorption bonds on graphitic and silicate surfaces implies overcoming activation barriers (Jeloaica & Sidis 1999; Sha et al. 2005a; Bonfanti et al. 2015; Goumans et al. 2009; Martinazzo

& Tantardini 2006). Theoretical works on the chemisorption of hydrogen atoms on silicate surfaces seem to show at first large discrepancies in the energy barrier and binding energy. Garcia-Gil et al. (2013) computed via a first-principle computation the interaction of H with the (010) surface of forsterite (Mg_2SiO_4). By overcoming an activation barrier, H can attach either to a shallow chemisorption (1880 K, 162 meV) site after overcoming a small barrier of 290 K (25 meV), or to a deep chemisorption site with an absorption energy of 7775 K (670 meV) and a barrier of 1880 K (162 meV). Oueslati et al. (2015) performed density functional calculations with different Mg-rich olivine nano-clusters and concluded that there is a distribution of chemisorption sites with binding energy ranging from 8000 up to 30000 K, see also Kerkeni & Bromley (2013). They demonstrated a linear dependency (Bell-Evans-Polanyi principle) between the activation energy for chemisorption E_{act} and the binding energy (E_b) and found a relationship between the H_2 reaction barrier for the Langmuir-Hinshelwood mechanism and the binding energy, independent of silicate dust grain shape, size, crystallinity and composition. Different types of nano-crystals and crystal surfaces have different chemisorption sites. Oueslati et al. (2015) findings can explain the large range of binding and activation energies found in various researches (Goumans et al. 2009; Kerkeni & Bromley 2013; Navarro-Ruiz et al. 2014, 2015). H_2 formation via the encounter of a gas-phase H atom and a chemisorbed atom (Eley-Rideal process) proceeds without activation barrier (Navarro-Ruiz et al. 2015).

H_2 can also form by the abstraction of an H-atom from hydrogenated PAHs with a small or no activation barrier (Farebrother et al. 2000; Rutigliano et al. 2001; Bachellerie et al. 2007; Ivanovskaya et al. 2010; Hirama et al. 2004; Skov et al. 2014; Pasquini et al. 2016). The sticking of H-atoms on graphitic surfaces and PAHs is the first step in the H_2 formation process and has been studied since the 1960s (Sha et al. 2005b; Bonfanti et al. 2015; Ferullo et al. 2016). Dumont et al. (2008) studied the H_2 formation with a kinetic Monte-Carlo model.

The paper is organised as follows: in Sect. 2 we describe our H_2 and HD formation model. The analytical H_2 formation models are presented in 3. In Sect. 3 we describe the grid of cloud models and the standard DIANA model for the comparison between our model and the analytical formulations. In Sect. 5 we present the results and a discussion in our grid of models and conclude in Sect. 6.

2. H_2 and HD formation model

The H_2 and HD formation model on cold and warm dust grains follow that of Cazaux & Tielens (2002, 2004). H_2 formation on grain surfaces should occur for a wide range of grain temperatures. The binding energies of physisorbed species are between few 100 K up to few 1000 K. Chemisorbed species have binding energies of few 10,000 K. We take H_2 formation on PAHs (Sect. 2.7) and in the gas-phase (Sect. 2.8) into account.

Surface chemistry concepts are reviewed in Bonfanti & Martinazzo (2016). We introduce our notations and the notion of pseudo-species. Chemisorption sites are modeled by a pseudo-element named *, whose total elemental abundance is set by the number density of surface sites and the number of available grain surfaces, which itself depends on the grain size distribution. The pseudo-element * has also a pseudo-species counterpart *. The pseudo-species do not migrate nor desorb. Atomic hydrogen atoms (and deuterium atoms) can adsorb weakly on a physisorption site, hop to a neighboring site or attempt to overcome a barrier to reach a strongly bound chemisorption site.

Atoms can also diffuse between chemisorption sites or go to a physisorption site if they can overcome the activation barriers.

H₂ and HD formation occur via the Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms on dust grains and PAHs for physisorbed and chemisorbed species.

We assume that each physisorption site is associated with a chemisorption site. The physisorbed atoms are designated by H# and D#. The model includes the most abundant gas- and surface-species as listed in Table D.3. A chemisorbed atom is assigned a star * in front of it. Chemisorbed H and D are thus called *H# and *D# respectively. The pseudo-elemental conservation reads $[*] + [*H\#] + [*D\#] = n_* + n_{*H\#} + n_{*D\#} = n_{\text{surf,chem}}$, where $n_{\text{surf,chem}} = 4\pi N_{\text{surf}} r^2 n_d$ is the number density of chemisorption sites (N_{surf} is the surface density of physisorption and chemisorption sites and is equal to $1.5 \times 10^{15} \text{ cm}^{-2}$, $n_{\text{site}} = 4\pi N_{\text{surf}} r^2$ is the number of adsorption sites per monolayer, r is the grain mean radius, and n_d is the number density of dust grains in cm^{-3}). We adopted a treatment by rate reactions since the densities in disks are high ($n_H > 10^4 \text{ cm}^{-3}$). The main surface reactions are listed in Table D.2. Table F.1 and F.2 list the main variables used in this study.

2.1. Adsorption and sticking

Most of the processes in our model follow the work of Hasegawa et al. (1992). The first process is the adsorption and desorption of atomic hydrogen or deuterium from the grain surfaces. A gas-phase atom or molecule i (in this paper $i=H, D, \text{PAH}, \dots$) adsorbs on a surface physisorption (unlimited number) or a chemisorption (limited number) site at the general rate

$$R_i^{\text{ads}} = 4\pi r^2 \bar{v}_i f_{\text{avail}} n_d S_i Q_{\text{Bell}}(a_i^{\text{act}}, E_i^{\text{act}}, T_g) s^{-1}, \quad (1)$$

where $4\pi r^2$ in cm^2 is the grain surface area (r is the grain radius), $\bar{v}_i = (kT_g/(2\pi m_i))^{1/2}$ is the thermal speed in cm s^{-1} , n_d is the number density of dust grains in cm^{-3} , and S_i is the sticking coefficient. The fraction of available sites f_{avail} is unity for physisorption and equal to the fraction of unoccupied sites for chemisorption ($f_{\text{avail}} = n_*/n_{\text{surf,chem}}$). Q_{Bell} is the transfer function (see Sect. 2.1.2). The treatment of the physisorption and chemisorption differs. The sticking coefficient depends on the surface and type of adsorption (Jones & Williams 1985).

2.1.1. Physisorption

There is no activation energy for physisorption ($Q_{\text{Bell}}=1$). Hollenbach & McKee (1979) proposed for the sticking coefficient of H the following formula

$$S_{\text{phys}}^{-1} = 1 + 0.4 \times \left(\frac{T_g + T_d}{100} \right)^{0.5} + 0.2 \times \frac{T_g}{100} + 0.08 \times \left(\frac{T_g}{100} \right)^2. \quad (2)$$

The adsorption rate on physisorption sites (eq. 1) simplifies to

$$R_i^{\text{gp}} = 4\pi r^2 \bar{v}_i^{\text{th}} n_d S_{\text{phys}} s^{-1}. \quad (3)$$

We assume that the number of physisorption sites per grain remains constant as the ice mantle grows and that the mean grain radius r is not changed. The sticking of atomic hydrogen on water ice has been recently studied (Veeraghattam et al. 2014) while Chaabouni et al. (2012) computed the sticking coefficient of H and D atoms onto silicate surfaces.

2.1.2. Eley-Rideal chemisorption

In the precursor-mediated adsorption mechanism, an atom adsorbs first without barrier to a weak physisorption site. This atom can subsequently diffuse to a deeper chemisorption site with small activation barrier ($\#H + * \rightarrow \#H^*$). The direct mechanism involves the gas-phase hydrogen (deuterium) atoms impinging on the surface and overcoming directly the activation barrier ($E_i^{\text{gc}} > 1000 \text{ K}$). Theoretical studies on these two mechanisms do not show actual decrease of the activation barrier when the atom is already physisorbed for silicate grains (Navarro-Ruiz et al. 2014). The chemisorption is of C1- type whereby the H_{chem}^+ is bonded to an O anion and a negative charge is transferred to a nearby Mg cation (Kerkeni et al. 2017). We treat the formation of a chemisorption bond from an impinging gas-phase H-atom (D-atom) as an activated Eley-Rideal process with rate R_i^{gc}

$$R_i^{\text{gc}} = \sqrt{\frac{kT_g}{2\pi m_i}} \frac{Q_i^{\text{gc}}}{N_{\text{surf}}} n_* S_{\text{chem}} s^{-1}, \quad (4)$$

with the Bell's rate being $Q_i^{\text{gc}} = Q_{\text{Bell}}(a_i^{\text{gc}}, E_i^{\text{gc}}, T_g)$, N_{surf} is the number density of surface sites (in cm^{-2}), and n_* the number density of chemisorption sites (cm^{-3}). The probability to overcome an adsorption activation barrier for chemisorption is described by a tunnelling-corrected Arrhenius formula called Bell's formula (Bell 1980):

$$Q_{\text{Bell}}(a_i^{\text{gc}}, E_i^{\text{gc}}, T_g) = \frac{\beta \exp(-\alpha) - \alpha \exp(-\beta)}{\beta - \alpha}, \quad (5)$$

where

$$\alpha = E_i^{\text{gc}}/kT_g, \quad (6)$$

and

$$\beta = \frac{4\pi a_i^{\text{gc}}}{h} \sqrt{2m_i E_i^{\text{gc}}}. \quad (7)$$

m_i is the mass of the impinging species (m_H for H or m_D for D). a_i^{gc} is the width of the activation barrier assuming a rectangular-shaped barrier of height E_i^{gc} , and h is the Planck constant. The Bell's formula is non-dimensional and reduces to the thermal term when tunnelling does not occur ($a_i^{\text{gc}} \rightarrow \infty$). It has been used successfully to model gas-phase rates when direct tunnelling effect occurs.

One can determine a temperature T_q below which quantum tunnelling effect dominates by equating α with β for a general process with an activation barrier:

$$T_q = \left(\frac{E_{\text{act}}}{k} \right) \left(\frac{h}{4\pi a_{\text{A}} \sqrt{2m_{\text{amu}} E_{\text{act}}}} \right) = 2.46243 \left(\frac{E_{\text{act}}}{a_{\text{A}}^2 m_{\text{amu}}} \right)^{1/2}, \quad (8)$$

where E_{act} is the activation energy in Kelvin, a_{A} is the barrier width in Å, and m_{amu} is the mass of the tunnelling species in atomic mass units. The assumed value of the barrier width a_{A} has a stronger impact on the species diffusion rate than the mass or diffusion energy, for which only the square root of the value counts, at low surface temperature.

The barrier width for H-atom (and D-atom) Eley-Rideal chemisorption is assumed to be 0.5 Å. The sticking coefficient S plays a major role at high dust temperature in controlling the chemisorption (Cazaux et al. 2011). Both sticking coefficients account for the effect of gas and dust temperatures.

The inverse of the surface density of sites N_{surf} is a typical surface site cross-section ($\sigma_{\text{surf,site}} = 1/N_{\text{surf}} \simeq 1/1.5 \times 10^{15} \text{ cm}^2$),

$n_* = 4\pi r^2 f_{\text{avail}} n_d N_{\text{surf}} \leq n_{\text{surf,chem}}$ is the number density of unoccupied chemisorption sites. When the surface is covered by more than N_{layer} layers, the ER chemisorption rate is set to zero ($R_i^{\text{gc}} = 0$). The standard value used in our models for N_{act} is two.

For chemisorption, we use the sticking coefficient of Cuppen et al. (2010); Sha et al. (2005a)

$$S_{\text{chem}} = (1 + 5 \times 10^{-2} \sqrt{T_g + T_d} + 1 \times 10^{-14} T_g^4)^{-1}. \quad (9)$$

with temperatures in K.

2.1.3. Adsorption rate coefficients

The rate coefficients are

$$dn_{\#,i}/dt = R_i^{\text{gp}} n_i \text{ cm}^{-3} \text{ s}^{-1}, \quad (10)$$

for physisorption and

$$dn_{*,i}/dt = R_i^{\text{gc}} n_i \text{ cm}^{-3} \text{ s}^{-1} \quad (11)$$

for Eley-Rideal chemisorption.

2.2. Desorption

An adsorbed species can thermally desorb, or desorb after the absorption of a UV photon, or after a cosmic ray has crossed the grain and deposited some energy. Desorption can be an activated process and is endothermic. The desorption energy is defined as

$$E_i^{\text{des}} = E_i^{\text{b}} + E_i^{\text{des,act}} \text{ ergs}. \quad (12)$$

For physisorption, which is non dissociative, there is no barrier ($E_i^{\text{des,act}}=0$) and the desorption and binding energy E_i^{b} are equal. The binding energy E_i^{b} is in principle not unique but follows a distribution of values. Breaking of a chemisorption bond involves an activation energy equal to the chemisorption activation energy. The thermal desorption rate is

$$R_i^{\text{cg,th}} = \nu_{0,i} Q_{\text{Bell}}(a_i^{\text{des,act}}, E_i^{\text{des,act}}, T_d) e^{-E_i^{\text{b}}/kT_d} \text{ in s}^{-1}, \quad (13)$$

The frequency is given by the formula for a rectangular barrier of width a_c and height E_{act}

$$\nu_{0,i} = \sqrt{\frac{2N_{\text{surf}} E_i^{\text{b}}}{\pi^2 m_i}}. \quad (14)$$

We derived a frequency $\nu_{0,i}$ of $(1-10) \times 10^{12}$ Hz assuming a surface site density $N_{\text{surf}} = 1.5 \times 10^{15}$ sites cm^{-2} . Only desorption from chemisorption sites are activated $Q_{\text{Bell}}(a_i^{\text{des,act}}, E_i^{\text{des,act}}, T_d) = Q_i^{\text{cg}} = Q_i^{\text{gc}}$. For desorption from physisorption sites $Q_{\text{Bell}}(a_i^{\text{des,act}}, E_i^{\text{des,act}}, T_d)=1$, thus

$$R_i^{\text{pg,th}} = \nu_{0,i} e^{-E_i^{\text{b}}/kT_d} \text{ in s}^{-1}, \quad (15)$$

The total desorption rate for species i includes cosmic-ray hit induced desorption and is assumed to follow a first-order desorption process. It reads for the physisorbed species

$$R_i^{\text{des,pg}} = R_i^{\text{pg,th}} + R_i^{\text{pg,ph}} + R_i^{\text{pg,CR}}, \quad (16)$$

and for the chemisorbed species

$$R_i^{\text{des,cg}} = R_i^{\text{cg,th}} + R_i^{\text{cg,ph}} + R_i^{\text{cg,CR}} \text{ s}^{-1}. \quad (17)$$

The desorption for species i reads

$$dn_i/dt = R_i^{\text{des,pg}} n_i^{\text{act}} + R_i^{\text{des,cg}} n_{*,i} \text{ cm}^{-3} \text{ s}^{-1}. \quad (18)$$

For physisorbed species the concentration of active surface species i is

$$n_i^{\text{act}} = n_i \text{ if } n_{\#, \text{tot}} \leq nb_{\text{site}} n_d \\ = n_i (N_{\text{act}}/N_{\text{layer}}) \text{ if } n_{\#, \text{tot}} > nb_{\text{site}} n_d, \quad (19)$$

where the number of physisorbed layers on a dust grain is $N_{\text{layer}} = n_{\#, \text{tot}}/(n_d nb_{\text{site}})$. $n_{\#, \text{tot}} = \sum_j n_{\#,j}$ is the total number density of physisorbed species and N_{surf} is the number of sites per monolayer. N_{act} is the number of chemically physisorption active layers and is a free parameter of the model. All chemisorbed species can desorb since we restrict the maximum number of chemisorption layers to one.

Photodesorption is accounted for either through a factor that scales with the interstellar UV field (0D model) or using the actual computed UV field obtained by detailed radiative transfer and photodissociation cross-sections (2D disk models). The photodesorption rate of physisorbed species i is given by

$$R_i^{\text{pg,ph}} = \pi r^2 \frac{n_d}{n_{\text{act}}} Y_i \chi F_{\text{Draine}} \text{ s}^{-1}, \quad (20)$$

where Y_i is the photo-desorption yield, $\chi F_{\text{Draine}} = 1.9921 \times 10^8$ photons/ cm^2/s is a flux-like measure of the local UV energy density computed from continuum radiative transfer (e.g., Woitke et al. 2009). We assume that photodesorption affects chemisorbed species the same way with rate $R_i^{\text{cg,ph}}$.

Cosmic-ray induced desorption follows the treatment of Hasegawa & Herbst (1993).

$$R_i^{\text{pg,CR}} = f(70\text{K}) R_i^{\text{pg,th}}(70\text{K}) \frac{\zeta_{\text{CR}}}{5 \times 10^{-17}} \text{ s}^{-1}, \quad (21)$$

where ζ_{CR} is the cosmic ray ionisation rate of H_2 , $f(70\text{K}) = 3.16 \times 10^{-19}$ the 'duty-cycle' of the grain at 70 K and $R_i^{\text{des,th}}(70\text{K})$ the thermal desorption rate for species i at temperature $T_d = 70\text{K}$. The adopted value for $f(70\text{K})$ is strictly valid only for $0.1 \mu\text{m}$ grains in dense molecular clouds. Explosive desorption were not considered and will be included in future works (Ivlev et al. 2015). The dust temperature after a Cosmic-Ray hit is not high enough to desorb a species in a chemisorption site.

2.3. Thermal and tunnelling surface diffusion

On grain surfaces the diffusive movement of H atoms from one site to another site occurs either by thermal hopping when there is sufficient energy to overcome the energy barrier or by tunnelling. Diffusion can be viewed as a random walk process. Atoms on a physisorption site can hop to another such site or to a deeper chemisorption site after overcoming an activation barrier (Barlow & Silk 1976; Leitch-Devlin & Williams 1984; Tielens & Allamandola 1987). A H-atom in a chemisorption site needs to overcome the energy difference between a physisorption and a chemisorption site in addition to the activation barrier in order to move to a physisorption site (Aronowitz & Chang 1980). We use again the Bell's formula to model the surface diffusion tunnelling effects

$$R_i^{\text{diff,th}} = \nu_{0,i} Q_i^{\text{diff}}(a_i^{\text{diff}}, E_i^{\text{diff}}) e^{-\Delta E_{ij}/kT_d} / nb_{\text{site}} \text{ in s}^{-1}. \quad (22)$$

The factor Q_i^{diff} is the Bell formula (eq. 5) with

$$\alpha = E_i^{\text{diff}}/kT \quad (23)$$

and

$$\beta = \frac{4\pi a_i^{\text{diff}}}{h} \sqrt{2mE_i^{\text{diff}}}. \quad (24)$$

ΔE_{if} is the binding energy difference between the two adsorption sites:

$$\begin{aligned} \Delta E_{if} &= 0 & \text{if } E_i^b \leq E_f^b, \\ \Delta E_{if} &= E_i^b - E_f^b & \text{otherwise.} \end{aligned} \quad (25)$$

Thus $\Delta E = 0$ for hopping between two physisorption sites or between two chemisorption sites. m is the mass of the diffusing species. α corresponds to the thermal diffusion (hopping) while β refers to the quantum tunnelling. The diffusion time t_i^{diff} is the inverse of R_i^{diff} . The surface diffusion rates for species i are defined as the combination of thermal, tunnelling and cosmic-ray induced diffusion

$$R_i^{\text{diff}} = R_i^{\text{diff,th}} + R_i^{\text{diff,CR}} \text{ s}^{-1}, \quad (26)$$

where the cosmic-ray induced diffusion rate is (Hasegawa & Herbst 1993; Reboussin et al. 2014)

$$R_i^{\text{diff,CR}} = f(70\text{K}) R_i^{\text{diff,th}}(70\text{K}) \frac{\zeta_{\text{CR}}}{5 \times 10^{-17}} \text{ s}^{-1}. \quad (27)$$

An atom bound at a physisorption site can diffuse to another physisorption site, desorb, or land on the chemisorption site associated with the current physisorption site (Cazaux & Tielens 2002, 2004). This view is valid when the current physisorption site is related to a silicate or carbonaceous surface, i.e. when the surface has fewer than a monolayer of ice. In denser regions, multi-layer ice mantle can be built rapidly. When the grain has one or more monolayers, the H-atom can only physisorb on the ice mantle, e.g. water ice. In this case we assume that a physisorbed H/D-atom can still diffuse through the bulk of the ice mantle but at a lower diffusion rate than on the ice mantle surface and overcome the barrier to land on an available chemisorption site. The diffusion rates state that bulk diffusion is permitted so that as the ice mantle grows, the number of sites available for scanning also increases, independently of the assumed number of active layers. The reactions compete explicitly with the desorption processes (thermal, cosmic-ray induced, and photodesorption). Their respective rates concern the active species. The process is formally represented as



and



The diffusion of species i is restricted to the physisorption active layers similar to the desorption

$$dn(i)/dt = R_i^{\text{diff}} n_i^{\text{act}}(i) \text{ cm}^{-3} \text{ s}^{-1}. \quad (30)$$

An alternative interpretation of our assumption is that the average diffusion rate for all the species on the surface and in the bulk is lower by a factor $N_{\text{act}}/N_{\text{layer}}$ when there is more than one monolayer.

2.4. The rate equation treatment

Since we focus on H₂ and HD formation in dense cold and warm regions, we adopted the rate equation treatment for the surface chemistry.

2.4.1. Langmuir-Hinshelwood reactions

The Langmuir-Hinshelwood surface reaction prescription follows the implementation (Hasegawa et al. 1992). The surface reaction rate coefficient k_{ij} (in cm³ s⁻¹) between surface adspecies i and j with respective number density n_i and n_j is the probability of reaction per encounter (κ_{ij}) times the rate of encounter between the two species scanning the surface:

$$k_{ij} = \kappa_{ij}(R_i^{\text{diff}} + R_j^{\text{diff}})/n_d \text{ cm}^3 \text{ s}^{-1}, \quad (31)$$

where κ_{ij} is the probability for the reaction to occur upon encounter between species i and j after both have diffused on the grain mantle, R_i^{diff} and R_j^{diff} (in s⁻¹) are the diffusion rates for species i and j , and n_d (in cm⁻³) is the number density of dust grains. We assume that the newly-formed H₂ desorb immediately because of the high exothermicity of the reaction. The probability for the reaction to occur κ_{ij} follows a competition between association of the two species, modeled by the Bell formulation to account for thermal crossing and tunnelling of potential activation barrier, and diffusion (Bonfanti & Martinazzo 2016; Garrod & Pauly 2011; Ruaud et al. 2016):

$$\kappa_{ij} = \frac{Q_{\text{Bell}}(a_{ij}^r, E_i^{\text{act}})}{Q_{\text{Bell}}(a_r, E_i^{\text{act}}) + P_i^{\text{diff}} + P_j^{\text{diff}}}, \quad (32)$$

where a_{ij}^r is the width of the barrier and E_i^{act} the activation barrier height (energy), $P_i^{\text{diff}} = R_i^{\text{diff}}/\nu_{0,i}$. The mass used in the Bell formula is that of the lighter species. When no competition is accounted for the probability is

$$\kappa'_{ij} = \nu_{0,i} Q_{\text{Bell}}(a_{ij}^r, E_i^{\text{act}}), \quad (33)$$

For barrierless reactions, $\kappa_{ij} = 1$ and $\kappa'_{ij} = 1$, and the rate becomes

$$k_{ij} \simeq (R_i^{\text{diff}} + R_j^{\text{diff}})/n_d \text{ cm}^3 \text{ s}^{-1}, \quad (34)$$

When $E_i^{\text{act}} \ll E_i^{\text{diff}}, E_j^{\text{diff}}$ and without tunnelling effects $\kappa_{ij} \rightarrow 1$ and the rate tends towards the diffusion-limited rate

$$k_{ij} \simeq (R_i^{\text{diff}} + R_j^{\text{diff}})/n_d \text{ cm}^3 \text{ s}^{-1}, \quad (35)$$

while without competition the rate is

$$k'_{ij} = \nu_{0,i} Q_{\text{Bell}}(a_{ij}^r, E_i^{\text{act}})(R_i^{\text{diff}} + R_j^{\text{diff}})/n_d \text{ cm}^3 \text{ s}^{-1}. \quad (36)$$

In that case, $k_{ij} \gg k'_{ij}$. On the other hand, when $E_i^{\text{act}} \gg (E_i^{\text{diff}}, E_j^{\text{diff}})$, the diffusion terms (R_i^{diff} and R_j^{diff}) dominate and cancel out in the rate coefficient (since the diffusion terms are present as numerator and denominator), which becomes

$$k_{ij} \simeq \nu_{0,i} Q_{\text{Bell}}(a_{ij}^r, E_i^{\text{act}})/n_d \text{ cm}^3 \text{ s}^{-1}, \quad (37)$$

and again $k_{ij} \gg k'_{ij}$. The diffusion is so fast that the reactants are always in the situation where the recombination (association) can occur.

The barrier for H diffusion from a physisorption site to another one in Kelvin is between 256 K (Kuwahata et al. 2015) to 341 K (Congiu et al. 2014) whereas the barrier for H₂ formation is 250 K or less (Navarro-Ruiz et al. 2014). We adopted a barrierless H₂ recombination between two physisorbed H atoms.

At $10 < T_d < 20$ K and assuming comparable diffusion and association (reaction) activation energy and weak photodissociation, the probability of reaction becomes $\kappa_{ij} \simeq 1/3$. At low

temperature ($T_d < 10$ K), thermal processes become insignificantly slow and both the diffusion and reaction rates are dominated by tunnelling. Diffusion tunnelling of H-atoms has a large barrier width of ~ 3.9 Å compared to ~ 0.5 Å for reaction barrier (Limbach et al. 2006) such that the reactive tunnelling rate dominates at $T_d < 10$ K, the probability of reaction becomes $\kappa_{ij} \simeq 1$. Therefore the H_2 formation rate below 20 K by recombination of physisorbed H-atom is diffusion limited even if a small barrier exists. We do not restrict H_2 formation by recombination of physisorbed H-atoms (LH mechanism) even when the surface is covered by a layer of physisorbed H-atom (Gavilan et al. 2012).

2.4.2. Eley-Rideal reactions

According to the semi-equilibrium theory, the probability of a gas-phase radical recombining with an atom located in an adsorption site is equal to the probability of the gas atom directly impinging on the occupied site multiplied by the probability of the gas atom having enough kinetic energy to overcome the reaction barrier, if any, with the possibility to tunnel through the barrier. Due to the long-range attractive potential, the impinging species has an energy of $1/2kT_g + E_i^b$ relative to the surface species (E_i^b is the binding energy). Part of this energy can be used to overcome a reaction barrier.

Laboratory and theoretical works suggest that the formation of H_2 via ER process is barrierless (or has a very small barrier) both on silicate and carbonaceous surfaces. The Eley-Rideal formation of H_2 from an impinging H on a physisorbed or chemisorbed H-atom has a rate of

$$R_{H_2}^{gp} = \sqrt{\frac{kT_g}{2\pi m_H}} \frac{1}{N_{surf}} n_{H\#} = 2.425 \times 10^{-12} \sqrt{T_g n_{H\#}} s^{-1}. \quad (38)$$

and

$$R_{H_2}^{gc} = \sqrt{\frac{kT_g}{2\pi m_H}} \frac{1}{N_{surf}} n_{*H\#} s^{-1}. \quad (39)$$

For HD, the rate is composed of two terms, one is the rate when a gas phase atom hits a chemisorbed D-atom and the second when a D-atom hits a chemisorbed H atom. The rate $R_{H_2}^{gc}$ is null when there is more than N_{layer} of ice, i.e. the water-ice mantle shield the chemisorbed H-atoms from being directly hit by a gas-phase atom.

2.5. Diffusion-mediated chemisorption

As the direct Eley-Rideal chemisorption is hampered by the presence of water ice mantle below the water sublimation (between 90 and 150 K depending on the gas density), chemisorption mostly occurs after a H-atom has diffused through the mantle and reached the interface between the mantle and the refractory surface. The diffusion rate in the bulk is decreased by the total number of ice layers. This is an extremely simple method to model a slower diffusion in the ice mantle compared to the diffusion at the ice surface. At the interface, the H-atom can overcome the barrier to chemisorption. The rate for this reaction is

$$R_{H\#}^{pc} = \kappa_{H\#}^{pc} R_{H\#}^{diff} (n_*/n_d) s^{-1}. \quad (40)$$

This rate should be compared to the thermal-dominated desorption rate of the physisorbed H-atom

$$R_{H\#}^{pg} = \nu_{pg} e^{-E_{H\#}^b/kT_d} s^{-1}. \quad (41)$$

In the thermal regime ($T_d > T_d = 78$ K), the lowest activation barrier for chemisorption is $E_{H\#}^{act} \sim 900$ –1000 K on silicate (Oueslati et al. 2015) compared to a diffusion energy of $\simeq 406$ K (Perets et al. 2007) and an adsorption energy of $\simeq 510$ K. The diffusion-mediated chemisorption rate is reaction-limited

$$R_{H\#}^{pc} = \nu_{H\#}^{pc} Q_{H\#}^{pc} (n_*/n_d) \simeq \nu_{H\#}^{pc} e^{-E_{H\#}^{act}/kT_d} (n_*/n_d) s^{-1} \quad (42)$$

The activation barrier to form H_2 from the encounter of a physisorbed and a chemisorbed atom is the same as the barrier to form a chemisorption bond because both processes involve the breaking of the H chemical bond to the surface. The rate per gas volume is

$$dn_{*H\#}/dt = R_{H\#}^{pc} n_H^{act} cm^{-3} s^{-1}. \quad (43)$$

The reverse mechanism is a chemisorbed H-atom escaping the deep well to reach a physisorption site $R_{*H\#}^{cp}$. The formation of H_2 can happen after a H-atom ($H\#$) hops from a physisorption site to a site occupied by a chemisorbed H-atom with number density $n_{*H\#}$, the rate is

$$R_{H\#,*H\#} = R_{H\#}^{diff} (n_{*H\#}/n_d) s^{-1}. \quad (44)$$

2.6. Reactions involving PAHs

PAHs are not formed or destroyed in our chemical network and only exchange charges with other positively-charged species (for examples H^+ , He^+ , Mg^+ , Fe^+ , C^+ , Si^+ , S^+ , HCO^+ , ...) or can be hydrogenated ($PAH-H_x$, $PAH-H_x^+$, $PAH-H_xD$, $PAH-H_xD^+$). $PAH-H_x^+$ ($x=0, 1, \dots, 18$). The ionised $PAH-H_x$ s can recombine with a free electron. Chemical reaction rates involving PAHs are highly uncertain. Most of the rates are extrapolations from a few existing laboratory or theoretical rates and are discussed in Appendix B.

2.7. H_2 and HD formation on neutral and cationic PAHs

Experimental and theoretical studies on neutral hydrogenated PAHs (called here $PAH-H_x$, with $x=1, 2, \dots, 18$) suggest that H_2 can form through barrierless Eley-Rideal abstractions (Bauschlicher 1998; Mennella et al. 2012; Rauls & Hornekær 2008; Thrower et al. 2012). Morisset & Allouche (2008) computed quantum dynamically the sticking of a H atom on a graphite surface.

The H_2 formation proceeds in two steps. The first step is the hydrogenation of the PAHs or ionised PAHs, followed by H-abstraction. The adopted PAH is the large compact circumcoronene ($C_{54}H_{18}$), which has a peri-condensed stable structure (Tielens et al. 1987). Although the carbon backbone fragmentation efficiency upon absorption of a UV photon increases with the degree of hydrogenation (Wolf et al. 2016), we modeled hydrogenated PAHs up to $PAH-H_x$ with $x=18$ equal to the number of edge carbon for the circumcoronene.

We adopted a cross section of 1.1 Å^2 per reactive carbon atom for radiative hydrogen association (Boschman et al. 2015) together with a barrier E_i^{act}

$$k_{PAH-H_x,H} = 2.78 \times 10^{-11} (T_g/300)^{1/2} N_C Q_{Bell} (E_{PAH-H_x,H}^{act}) cm^3 s^{-1}, \quad (45)$$

where $Q_{Bell}(E_{PAH-H_x,H}^{act})$ is a Bell's formula (eq. 5), i.e. we consider that H-tunnelling is possible and $x \geq 0$. It is clear that hydrogenation of neutral PAHs is an activated process because the formation of a C-H bond requires a rehybridisation (sp² to

Table 1. PAH successive hydrogenation energy barriers ($E_{\text{PAH-H}_x\text{H}}^{\text{act}}/k$) in Kelvin. The adopted values are shown in bold face.

Hydrogenation level	outer edge	edge	center	Ref.
PAH-H	116	1740	2553	<i>a</i>
	692			<i>b</i>
	324			<i>c</i>
PAH-H ₂	348	2669	3365	<i>a</i>
	0			<i>b</i>
	0			<i>c</i>
PAH-H ₃	348			<i>b</i>
	533			<i>c</i>
PAH-H ₄	0			<i>b</i>
	0			<i>c</i>
PAH-H ₅	0			<i>b</i>
	742			<i>c</i>
PAH-H ₆	0			<i>b</i>
	0			<i>c</i>
PAH-H ₇	0			<i>b</i>
	406			<i>c</i>
PAH-H ₈	0			<i>b</i>
	0			<i>c</i>
PAH-H ₉	348			<i>c</i>
PAH-H ₁₀	0			<i>c</i>
PAH-H ₁₁	603			<i>c</i>
PAH-H ₁₂	0			<i>c</i>
PAH-H ₁₃	382			<i>c</i>
PAH-H ₁₄	0			<i>c</i>
PAH-H ₁₅	382			<i>c</i>
PAH-H ₁₆	0			<i>c</i>
PAH-H ₁₇	452			<i>c</i>
PAH-H ₁₈	0			<i>c</i>

Ref. ^aCazaux et al. (2016) for PAH cations; ^bRauls & Hornekær (2008); ^cBoschman et al. (2015), the values are for coronene C₂₄H₁₂.

sp³) of the carbon orbitals. Rauls & Hornekær (2008); Karlicky et al. (2014); Allouche et al. (2006) (see also Ferullo et al. 2016; Klose 1992) obtained a value of $E_{\text{PAH-H}_x\text{H}}^{\text{act}}/k=692$ K (0.06 eV). Other studies (Sha et al. 2005a) found barrier of 2321 K (0.2 eV). Aréou et al. (2011) found experimental evidence of a barrier.

Cazaux et al. (2016) and Rauls & Hornekær (2008) have studied the successive PAH hydrogenation barriers. The barrier energies depend on the type of attachment sites (outer edge site, an edge site, or a center site). Table 1 provides a summary of the values present in the literature. Computations (Rauls & Hornekær 2008) suggest that the barrier vanishes for high levels of hydrogenation. Boschman et al. (2015) modeled the PAH hydrogenation with alternate high and low barriers. We adopted the series of barrier energies from Boschman et al. (2015). Low energy barriers are central to permit H₂ formation at intermediate dust temperatures ($T_d=20-100$ K) when the chemisorption on silicate grains may be inefficient.

De-hydrogenation of PAH-H_x ($x \geq 1$), occurs mostly by photodissociation. The photodissociation threshold for hydrogenated circumcoronene (E_{th}) is equal to the binding energy (Andrews et al. 2016). Computations of the binding energies depend on whether H is chemisorbed to an edge carbon (C_{edge}) or not (C_{graph}), see e.g., Ferullo et al. (2016); Rasmussen (2013). When it is attached to a C_{graph} atom, the binding energy is ~ 0.6 eV. An atom attached to an edge carbon is more strongly bound (1–2 eV). The binding energy was found for H and D on graphite to be 0.6 (6963 K) and 0.95 eV (11024 K) (Zecho et al.

2002) and Ferro et al. (2003). The chemisorption site for H atom, located on the top of a C_{graph} carbon atom, has an energy of 0.57 eV (6847 K) for coronene C₂₄H₁₂ (Jeloaica & Sidis 1999) and weak binding site with 0.040 eV (464 K) may exist (Ma et al. 2011). Haruyama & Watanabe (2011) found a binding energy of pyrene C₁₆H₁₀ of 0.6 eV. Ferullo et al. (2016) used an improved density function theory model and computed for a chemisorption binding on an edge carbon of 2 eV for anthracene. In this study the adsorption (binding) energies of an H-atom on a C_{edge} atom of a PAH are taken from Klærke et al. (2013); Bauschlicher & Ricca (2014). For circumcoronene the binding energy E_0 of an extra H-atom in a C-H bond is ~ 1.4 eV (16250 K).

The unimolecular thermal dissociation rate of a PAH-H_x at an effective temperature T_e follows an Arrhenius approximation to the Rice-Ramsperger-Kassel-Marcus (RRKM) model (Jochims et al. 1994):

$$R_{\text{PAH-H}_x, T_e} = R_0(T_e) \exp(-E_0/kT_e) \text{ s}^{-1}, \quad (46)$$

where T_e is an effective temperature for a PAH with N_C carbon atoms upon absorption of a photon of energy $h\nu$ in eV (Tielens 2005):

$$T_e \simeq 2000 \left(\frac{h\nu}{N_C} \right)^{0.4} \left(1 - 0.2 \left(\frac{E_0}{h\nu} \right) \right). \quad (47)$$

The pre-exponential factor $R_0(T_e) = (kT_e/h) \exp(1 + (\Delta S/R)) \text{ s}^{-1}$ (Reitsma et al. 2014), where ΔS is the entropy change assumed to be 55.6 J K⁻¹ mol⁻¹ (Ling & Lifshitz 1998) and R is the gas constant.

Unimolecular dissociation competes with relaxation by the emission of infrared photons with a typical rate R_{IR} of 1 s⁻¹. The yield for photodissociation for $h\nu > E_0$ reads:

$$Y_{\text{PAH-H}_x, \text{UV}} = \frac{R_{\text{PAH-H}_x, T_e}}{R_{\text{PAH-H}_x, T_e} + R_{\text{IR}}}. \quad (48)$$

The yield is null for $h\nu < E_0$. The yield is used together with the PAH cross-section (Draine & Li 2001; Li & Draine 2001) and the local UV field spectrum to compute the actual photodissociation rate.

PAHs and hydrogenated PAHs can exchange IR photons with the dust grains and reach an average temperature T_{PAH} . In radiative thermal equilibrium T_{PAH} is equal to the dust grain temperature T_d in the optically thick midplane of protoplanetary disks (Woitke et al. 2016). Hydrogenated PAHs can undergo thermal unimolecular dissociation with the rate

$$R_{\text{PAH-H}_x, \text{therm}} = R_0(T_{\text{PAH}}) \exp(-E_0/kT_{\text{PAH}}) \text{ s}^{-1}. \quad (49)$$

An impinging H-atom can abstract the dangling H from a hydrogenated PAH-H_x to form H₂ (or PAH-H_xD to form HD) via a barrierless Eley-Rideal mechanism (Rauls & Hornekær 2008; Bauschlicher 1998). Cuppen & Hornekær (2008) model the H₂ formation by abstraction from hydrogenated graphite using the kinetic Monte-Carlo technique.

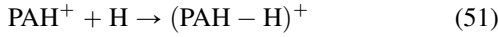
The cross-section for this reaction is 0.06 Å² per reactive carbon atom (Mennella et al. 2012) for neutral PAHs:

$$k_{\text{PAH-H}_x, \text{H}} = 1.5 \times 10^{-12} (T_g/300)^{1/2} N_C^{\text{react}} \text{ cm}^3 \text{ s}^{-1}. \quad (50)$$

$N_C^{\text{react}}=x$ for PAH-H_x, i.e. the rate scales with the number of extra hydrogens attached to the PAH. A small barrier (~ 10 meV, or ~ 115 K) may be present, but we chose to neglect it (Casolo et al. 2009). Petucci et al. (2018) computed a high energy of 1150 K for the barrier. Zecho et al. (2002) found that the D abstraction on low D-covered graphite bombarded with H-atoms

proceeds with a cross-section of up to 17 \AA^2 (and 4 \AA^2 at high coverage). Eley-Rideal cross sections around 4 \AA^2 have been also computed by Pasquini et al. (2016) using the quasi-classical trajectory method. The cross-sections do not show isotopic dependencies. Therefore, we adopted the same cross-section for H and D formation on hydrogenated PAHs using the cross-section measured in the experiments on amorphous carbon (a:C-H) by Mennella et al. (2012), which is however much lower than the values measured by Zecho et al. (2002) or computed by Pasquini et al. (2016). Duley (1996) adopted a cross section of 10 \AA^2 . On the other extreme, Skov et al. (2014) estimated an extremely low cross-section of 0.01 \AA^2 . We tested the effect of choosing a higher abstraction cross-section in appendix C.

PAH and hydrogenated PAHs can be ionised at low A_V and ionisation competes with photodissociation. A lower value of 0.02 \AA^2 has been reported by Oehrlein et al. (2010). The hydrogenation of PAH cations



proceeds without activation barrier or with a small barrier. Cazaux et al. (2016) computed a small barrier of 116 K (0.01 eV) for the first hydrogenation of coronene cation, consistent with the value of Hirama et al. (2004). The rate is quasi-independent on the size of the PAH (Demarais et al. 2014; Snow et al. 1998). We adopt therefore a size-independent rate:

$$k_{\text{PAH}-\text{H}_x^{n+},\text{H}} = 2 \times 10^{-10} (T_g/300)^{-3/2} Q_{\text{Bell}}(E_{\text{PAH}-\text{H}_x^{n+},\text{H}}^{\text{act}}) \text{ cm}^3 \text{ s}^{-1}, \quad (52)$$

with $E_{\text{PAH}-\text{H}_x^{n+},\text{H}}^{\text{act}} = 116 \text{ K}$. We further assume that the photodissociation of ionised hydrogenated PAHs follow the same rate as for the neutral PAHs.

H-abstraction reaction with cationic hydrogenated PAHs is a barrierless ion-neutral reaction. Therefore, the rate should be in the order of magnitude of a Langevin rate. We choose to use the scaling law of Montillaud et al. (2013):

$$k_{(\text{PAH}-\text{H}_x)^{n+}} = 1.4 \times 10^{-10} \left(\frac{N_H}{12} \right) \left(\frac{N_C}{24} \right)^{-1} \text{ cm}^3 \text{ s}^{-1}, \quad (53)$$

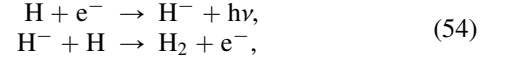
where N_H and N_C are the number of hydrogen and carbon atoms that constitute the PAH respectively and $n+$ is the charge of the PAH. The standard interstellar abundance of PAHs is 3×10^{-7} (Tielens 2005). In protoplanetary disks, a fraction f_{PAH} is still present. The H_2 formation efficiency depends on the charge of the PAH and hydrogenated PAHs. The recombination of $\text{PAH}-\text{H}^+$ follows the same rate as for PAH^+ apart that the recombination is dissociative $\text{PAH} - \text{H}^+ + \text{e}^- \rightarrow \text{PAH} + \text{H}$.

Hydrogen atoms can also physisorb on PAHs. The H_2 formation can be theoretically more efficient than formation from chemisorbed H atoms for graphite (Casolo et al. 2009). We have not considered H_2 formation from photodissociation of PAHs (Castellanos et al. 2018a,b). H diffusion can compete with desorption Borodin et al. (2011). In our model we assumed that H-atoms are too strongly bound for an efficient diffusion to another site for chemisorption.

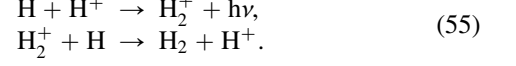
2.8. H_2 gas-phase formation and destruction

We incorporated in our H_2 and HD formation model the major formation and destruction routes for H_2 . Gas-phase H_2 reactions have been discussed by Glover (2003); Galli & Palla

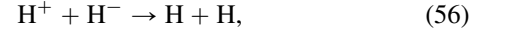
(1998). The formation occurs via H^- , whose electron can be ejected, carrying with it the excess heat of formation of 4.8 eV:



with rate for the later reaction from Launay et al. (1991); Martinez et al. (2009) and H^+ :



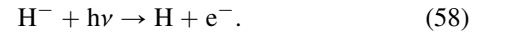
In both cases, the first step is a slow radiative recombination reactions. The hydrogen anions and cations are destroyed by mutual neutralisation (Moseley et al. 1970)



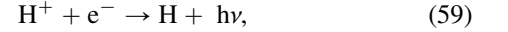
and H^+ can recombine with electron



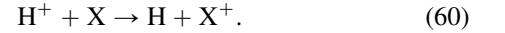
or the electron can be photodetached



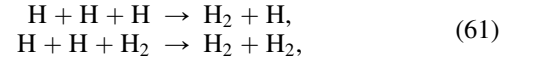
Protons are formed by charge exchange with He^+ or by ionisation by X-ray or cosmic rays. They can recombine or exchange the charge with a species X with ionisation potential lower than 13.6 eV:



or the electron can be photodetached



At density $> 10^8 \text{ cm}^{-3}$, three body reactions become important, when the third body carries the excess heat of formation in form of kinetic energy (Palla et al. 1983)

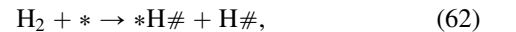


The rate coefficient for the first reaction is controversial (Forrey 2013b,a; Jacobs et al. 1967; Abel et al. 2002; Flower & Harris 2007; Palla et al. 1983) as it is a prime path to form H_2 in the Early Universe. Rates for the second reactions have been measured by Trainor et al. (1973) or modeled by Whitlock et al. (1974); Schwenke (1988, 1990).

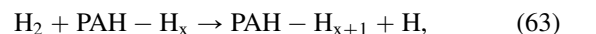
At very high gas densities and temperatures collision-induced dissociations (collider reactions) can occur (Ohlinger et al. 2007).

2.9. H_2 destruction by dissociative chemisorption

At high gas temperatures, H_2 impinging on bare silicate grain surfaces can dissociatively chemisorb. The model the process as two reactions



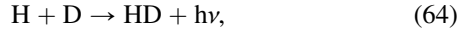
where we adopted a barrier height of 5802 K (Song & Xu 2016) for the first reaction with the rate using formula 4. The dissociative chemisorption of H_2 on PAH edges proceeds as



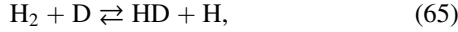
with a barrier height of 3481 K (Diño et al. 2004).

2.10. HD formation and destruction

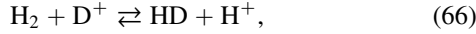
HD formation occurs both on grain surfaces, by abstraction of hydrogenated PAHs and by deuterium substitutions in the gas-phase (Cazaux & Spaans 2009). H₂ has a zero-point energy of 3135.5 K ($2179.3 \pm 0.1 \text{ cm}^{-1}$) and HD of 2719.7 K ($1890.3 \pm 0.2 \text{ cm}^{-1}$) resulting in an energy difference of $\Delta E^{\text{H}_2-\text{HD}} = 415.8 \text{ K}$ (Irikura 2007). The formation of HD occurs also in the gas-phase where exchange reactions can be efficient (Watson 1973; Brown & Rice 1986). Gas phase HD formation reactions have been discussed in the context of dust free or low-metallicity early Universe (Stancil et al. 1998; Galli & Palla 1998; Cazaux & Spaans 2009), cold molecular cloud by Roueff et al. (2007) and for PDR regions by Le Petit et al. (2002). The lower zero-point energy of the deuterated species translates into larger reaction activation energies. The radiative association



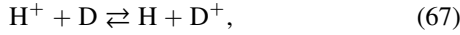
has an extremely low rate of $8 \times 10^{-27} \text{ cm}^3 \text{ s}^{-1}$ at 100 K (Stancil & Dalgarno 1997). In the gas-phase, HD can be formed efficiently at high temperature by the substitution reaction once H₂ has been formed (Mitchell & Le Roy 1973; Sun et al. 1980; Garrett & Truhlar 1980; Simbotin et al. 2011) by the reaction



which has a barrier of 3820 K. The backward reaction is endothermic by 420 K in the literature. We adopted an endothermicity of 415.8 K. The ion-neutral reaction



behaves unexpectedly with temperature (Smith et al. 1982; Honvault & Scribano 2013; González-Lezana et al. 2013; Lara et al. 2015) and follows a Langevin rate of $\sim 2.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ($k = 2.05 \times 10^{-9} (T/300)^{0.2417} \exp(-3.733/T_d) \text{ cm}^3 \text{ s}^{-1}$). The backward reaction is endothermic by 462 K. D⁺ is formed from H⁺ via



with an endothermicity of 41 K (Watson 1976). In region of low ionisation (low Cosmic Ray flux), this route may become inefficient. At low temperature, the rates of neutral-neutral reactions are negligible without tunnelling effects. Forward deuteration fractionation reactions are reversible with the forward reaction favoured because of the difference in zero-point energies.

H₂ and HD can be photodissociated and a self-shielding factor applies to both molecules with H₂ being much more shielded than HD (Le Petit et al. 2002; Thi et al. 2010).

2.11. Adopted data

The conclusions from our modeling depend on the choice of molecular data. It is believed that amorphous silicates can react with H (D) atoms more effectively and/or rapidly than crystalline silicates because they are thermodynamically unstable. Silicate surfaces show a distribution of chemisorption sites with binding energy ranging from $\sim 1000 \text{ K}$ to $\sim 20000 \text{ K}$ (Oueslati et al. 2015). The activation energy to overcome the barrier and chemisorb follows the Bell-Evans-Polanyi principle. As the dust grain temperature increases chemisorption sites with deeper potential are open so that we assume that a binding energy is $35 \times T_d$, knowing that the typical desorption occurs at $E_{\text{H}\#}^{\text{b}}/30 \text{ K}$ (Luna et al. 2017):

$$E_{\text{H}\#}^{\text{b}}/k = 35 \times T_d \text{ K}, \quad (68)$$

Table 2. Surface molecular data for physisorption processes.

Surface	E_i^{b}/k (K)	E_i^{diff}/k (K)	a_{db} (Å)
H atom			
Amorph. silicate	510 ^a	406 ^a	3.8 ^a
Amorph. ice	650 ^b	341 ^c	3.9 ^c
	607 ^d	516 ^d	
Poly-crystalline ice		256 ^e	
D atom			
Amorph. silicate	569 ^a	406 ^a	3.8 ^a
Amorph. ice	708 ^{b,f}	341 ^g	
Amorph. ice	665 ^d	415.8 ^d	
		255 ^h	
Poly-crystalline ice		267 ^e	

^aexp.:Perets et al. (2007); ^btheor.:Al-Halabi & van Dishoeck (2007); ^cexp.: from a fit to the data from Congiu et al. (2014); ^dexp.:Perets et al. (2005); ^eexp.:Kuwahata et al. (2015); ^fexp.:Matar et al. (2008);

with $\min(E_{\text{H}\#}^{\text{b}}/k) = 10,000 \text{ K}$ and $\max(E_{\text{H}\#}^{\text{b}}/k) = 25,000 \text{ K}$. We adopted a simple relation between the activation energy $E_{\text{H}\#}^{\text{act}}$ and the binding energy $E_{\text{H}\#}^{\text{b}}$

$$E_{\text{H}\#}^{\text{act}}/k = E_{\text{H}\#}^{\text{b}}/k - 9100 \text{ K}, \quad (69)$$

which gives an activation energy of $E_{\text{H}\#}^{\text{act}}/k = 900 \text{ K}$ for a binding of $E_{\text{H}\#}^{\text{b}}/k = 10,000 \text{ K}$. The lowest activation energy is consistent with the value of Cazaux & Tielens (2002). Both paths to form a chemisorbed H have the same barrier energy ($E_{\text{H}\#}^{\text{gc}} = E_{\text{H}\#}^{\text{pc}} = E_{\text{H}\#}^{\text{act}}$). The barrier energy for the reaction between a physisorbed and a chemisorbed H-atom is $E_{\text{H}\#,\text{H}\#} = E_{\text{H}\#}^{\text{act}}$. There is no barrier for the Eley-Rideal H₂ formation ($E_{\text{H}\#,\text{H}\#} = 0$) and the barrier is $E_{\text{H}\#,\text{H}\#} = 2E_{\text{H}\#}^{\text{act}}$ for H₂ formation from two chemisorbed atoms because it implies the breaking of two chemisorption bonds. For physisorption, there is also a variety of experimental and theoretical energies, which are summarized in Table 2. The diffusion barrier and the desorption energies for H atoms on amorphous silicate were taken from Perets et al. (2007). Hama et al. (2012) showed that there are many physisorption sites with a central energy of 22 meV. Ásgeirsson et al. (2017) have theoretically shown that a distribution of desorption (32–77 meV or 371–894 K) and diffusion (1–56 meV or 11–650 K) energies exist for H in an amorphous water ice matrix with a linear dependency of $E_{\text{H}\#}^{\text{diff}} = 0.68 E_{\text{H}\#}^{\text{b}}$. The theoretical results confirm the experiments where more than one energies have been found (Hama et al. 2012). Ásgeirsson et al. (2017) provide a possible explanation on the discrepancy between different experimental results (Manicò et al. 2001; Perets et al. 2005; Hornekar et al. 2003; Matar et al. 2008). At low H-coverage H is mostly adsorbed on the deep sites, while at high coverage the deep sites are occupied and H atoms seat on shallower sites. The distribution is narrower for crystalline ice.

The greater mass of D compared to H results in a smaller zero-point-energy and therefore in a larger binding energy. The binding energy for D atom is $\simeq 58 \text{ K}$ (5 meV) higher than the value for H atom (Le Petit et al. 2009). The diffusion energy barrier is not affected by the difference in zero-point-energy and $E_{\text{D}\#}^{\text{diff}} = E_{\text{H}\#}^{\text{diff}}$ since the zero-point-energy is accounted for in both the initial and final site.

Our choice of energies for physisorption is guided by: (1) a unique relatively high binding energy of $E_{\text{p}}^{\text{des}}/k = E_{\text{H}\#}^{\text{b}}/k = 600 \text{ K}$

whether H is attached on amorphous silicate or on amorphous water ice corresponding to a low coverage situation; (2) we adopted the scaling law of Ásgeirsson et al. (2017) and obtained $E_{H\#}^{\text{diff}}/k = 408$ K; (3) $E_{D_p}^{\text{des}}/k = E_p^{\text{des}}/k + 58 = 658$ K; (3) $E_{D\#}^{\text{diff}} = E_{H\#}^{\text{diff}} = 408$ K. The chemisorption binding energies for HD are also increased by 58 K from the values for H₂.

We illustrate the application of the Bell's formula to the tunnelling diffusion of physisorbed H-atoms. The physisorbed H-atom diffusion behaviour on cold grain surfaces is discussed in details in Congiu et al. (2014). In the Bell's formula, E_i^{diff} is the surface thermal diffusion in ergs. For physisorbed H-atoms we adopted a diffusion energy of 408 K. The barrier width to tunnelling $a_{H\#}^{\text{pp}}$ on amorphous water ice surface is found by matching the experimental data (Congiu et al. 2014) and a reasonable value is $a_{H\#}^{\text{pp}} = 3.9 \times 10^{-8}$ cm (3.9 Å). h is the Planck constant in erg s and m is the mass of the diffusing species in grams. The surface diffusion rate for H-atom $k_i^{\text{diff}} = \nu_0 Q_i^{\text{diff}}/N_{\text{surf}}$

ponent per volume, and S_H is the sticking coefficient, and ϵ is the recombination efficiency. The formula can be derived from the steady-state balance between formation and destruction of physisorbed H-atom H#

$$dn_{H\#}/dt = R_H^{\text{ads}} n_H - R_p^{\text{des}} n_p - 2k_{H_2}^{\text{pp}} n_p n_p = 0 \quad (71)$$

and the H₂ formation rate is

$$(dn_{H_2}/dt)_{\text{form}} = k_{H_2} n_p n_p \text{ cm}^{-3} \text{ s}^{-1}. \quad (72)$$

At low temperatures and low UV field, we can neglect the desorption, and we obtain the formation rate density

$$(dn_{H_2}/dt)_{\text{form}} = \frac{1}{2} R_H^{\text{ads}} n_H \text{ cm}^{-3} \text{ s}^{-1}, \quad (73)$$

where n_H is the number density of atomic hydrogen in the gas (in cm⁻³). The rate density is strictly speaking an upper limit since H atoms have to adsorb first. For HD formation, we follow the model described in Cazaux & Spaans (2009) and the rate assumes the same efficiency as for H₂.

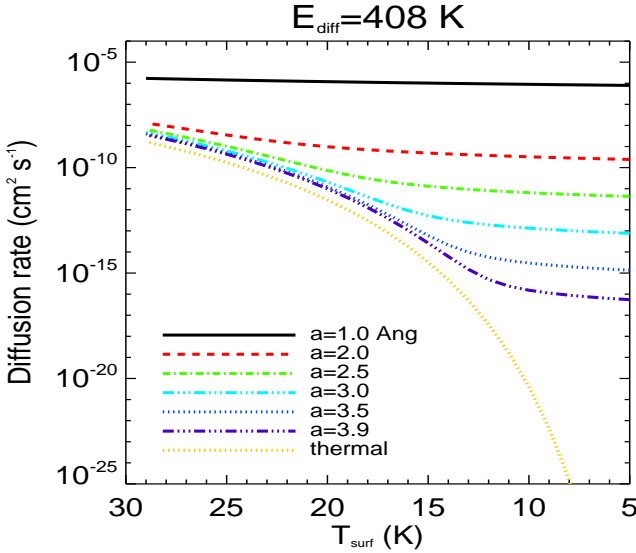


Fig. 1. Atomic hydrogen grain surface diffusion rate as function of the surface temperature for different values of the barrier width a in Å. In our model, we chose a value of 3.9 Å. The thermal diffusion rate is also shown.

(cm⁻² s⁻¹) is shown for different choices of the barrier width in Fig. 1. The figure also shows a purely thermal surface diffusion rate, which drops dramatically at low dust temperatures below $T_q = 11$ K from eq. 8.

3. Previous analytical H₂ formation models on silicate dust grains

3.1. Cazaux model

The standard analytical model for H₂ formation follows the model of Cazaux & Tielens (2002, 2004), which has been used since Hollenbach et al. (1971). The rate is

$$R_{H_2}^{\text{Cazaux}} \equiv \frac{1}{2} \epsilon 4\pi r^2 v_H^{\text{th}}(T_g) S_H n_d \equiv \frac{1}{2} R_H^{\text{ads}} \text{ s}^{-1}, \quad (70)$$

where $v_H^{\text{th}} = (kT_g/(2\pi m_H))^{1/2}$ is the thermal relative velocity of the hydrogen atom, $4\pi r^2$, n_d is the total surface of the dust com-

3.2. Jura's empirical H₂ formation rate coefficient

The H₂ formation (eq. 70) can be rewritten to recover the standard rate for H₂ formation, which has been measured by Jura (1974, 1975a,b). The observed rate has been derived from observations obtained by the Copernicus satellite in diffuse clouds and confirmed by Gry et al. (2002) using FUSE observations. First we define the average number of dust grains as

$$n_d = \frac{1.386 \text{ amu } n_{\langle H \rangle} \delta}{(4/3)\pi \rho_d r^3} \text{ cm}^{-3}, \quad (74)$$

which can be approximated by

$$n_d \approx 1.83 \times 10^{-15} n_{\langle H \rangle} \left(\frac{\mu \text{ m}^3}{r_{\mu \text{ m}}^3} \right) \left(\frac{\delta}{0.01} \right) \text{ cm}^{-3}, \quad (75)$$

where δ is the dust-to-gas mass ratio assumed to be 0.01 and the total gas number density is $n_{\langle H \rangle} = n_H + 2n_{H_2}$. We have assumed a silicate mass density ρ_d of 3.0 g cm⁻³. The number abundance of Helium is 0.096383, giving an extra mass to the gas of 0.386. For an average grain radius r of 0.1 micron and an efficiency of unity, we can find

$$R_{H_2} = 4.18 \times 10^{-18} S_H \sqrt{T_g} (0.1 \mu \text{ m}/r_{\mu \text{ m}}) n_{\langle H \rangle} \text{ s}^{-1}. \quad (76)$$

The formation rate does not explicit dependent on the dust temperature. The implicit assumption ($\epsilon=1$) is that all adsorbed H-atom will eventually leave the grains as H₂. The H₂ formation rate coefficient for a gas at 80 K as found in the diffuse interstellar medium, $r_{\mu \text{ m}} = 0.1 \mu \text{ m}$, and a sticking coefficient of unity, is

$$k_{H_2} = 3.74 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}, \quad (77)$$

which is consistent with the values found by Gry et al. (2002) between 3.1×10^{-17} and $4.5 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$. They confirmed the earlier results of Jura (1975a), who found a H₂ formation rate coefficient of $3.0 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$. Therefore, Jura's H₂ formation rate coefficient is compatible with the highest possible rate for H₂ formation on silicate dust grains. The empirical H₂ formation rate coefficient relies on a detailed knowledge of the H₂ photodissociation rate in the clouds.

Table 3. Cloud model parameters.

Parameter	symbol	values
Gas density	$n_{\langle H \rangle}$	$2 \times 10^4 \text{ cm}^{-3}$
Temperature	$T_d = T_g$	10 to 700 K
Extinction	A_V	10
Strength of interstellar UV	χ^{ISM}	1
Cosmic ray H_2 ionisation rate	ζ_{CR}	$1.7 \times 10^{-17} \text{ s}^{-1}$
Mean grain radius	r	10^{-5} cm
Dust-to-gas mass ratio	δ	0.01
PAH abundance rel. to ISM	f_{PAH}	1

Notes. $\chi^{\text{ISM}} = 1$ is the ISM Draine UV field. $f_{\text{PAH}} = 1$ corresponds to a PAH abundance of 3×10^{-7} .

4. ProDiMo chemical models

ProDiMo is a code built to model the gas and dust grain physics and chemistry (Woitke et al. 2009; Kamp et al. 2010; Woitke et al. 2016). It has been used to model disk Spectral Energy Distributions (SEDs, Thi et al. 2011), water deuteration chemistry (Thi et al. 2010) CO rovibrational emissions including UV-fluorescence (Thi et al. 2013), and many *Herschel* observations from the *GASPS* large programme (Dent et al. 2013). X-ray physics are implemented (Aresu et al. 2012; Meijerink et al. 2012; Aresu et al. 2011). A detailed discussion of the different physics and their implementations are given in the articles listed above. Here we summarize the main features. In our chemical modeling we included 116 gas and ice species, PAHs. Self-shielding against photodissociation for H_2 and HD is taken into account. Reaction rate coefficients that are not explicitly discussed in this paper are taken from UMIST2012 (McElroy et al. 2013). The adsorption energies are mixed from various sources (Aikawa et al. 1996; Garrod & Herbst (2006), and UMIST2012 (McElroy et al. 2013). The network was complemented by reactions relevant to high temperature conditions (Kamp et al. 2017). We used the chemistry solver in the ProDiMo code in a zero-dimensional model. Further modeling in the context of protoplanetary disks will be reported in subsequent articles. The assumptions are $T_d = T_g$, a fixed UV field strength and extinction A_V for the zero-dimensional model. We expanded the so-called small disk chemical network by including the species require modeling H_2 and HD formation (see Table AD.1). Only relevant surface and gas-phase chemical reactions are included, and they are listed in Tables D.2 and D.3. The later table lists reactions with singly-hydrogenated PAHs. Similar reactions with multiply-hydrogenated PAHs are used in the modeling but are not shown. The results of runs with multiply-hydrogenated PAHs are shown in appendix C. The elemental abundances are taken from Kamp et al. (2017) and in addition the adopted deuterium elemental abundance is 1.5×10^{-5} (Linsky et al. 1995).

Table 4. Cloud models.

#	Model	Physi-sorption	Chemi-sorption	Formation on PAHs
1	MC-ANALYTIC			
2	MC-PHYS	✓		
3	MC-PHYS-CHEM-PAH	✓	✓	✓

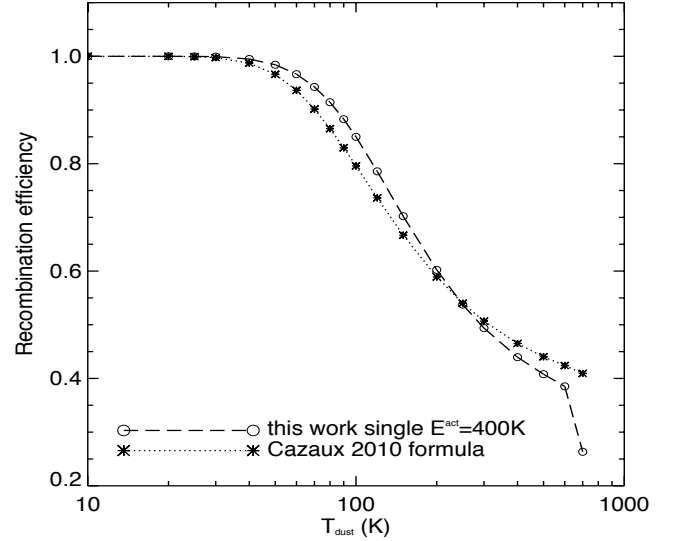


Fig. 2. Comparison between the analytic H_2 formation efficiency using and the formula from Cazaux & Tielens (2004) with the 2010 update (the binding energy for physisorbed H-atom $E_{H_p} = 600 \text{ K}$, and the saddle point $E_S = E_{H_p} - E^{\text{pc}} = 200 \text{ K}$, with E^{pc} being the activation energy to overcome to go from a physisorption site to a chemisorption site) and our numerical code for a zero-dimensional model.

5. Results & discussions

5.1. Analytical H_2 formation efficiency

The H_2 formation rate at all temperatures without considering the Eley-Rideal processes reads

$$(dn_{H_2}/dt)_{\text{LH}} = k^{\text{pp}} n_p n_p + k^{\text{pc}} n_p n_c + k^{\text{cc}} n_c n_c. \quad (78)$$

We assume that $E_{H\#, *H\#} = E_{H\#}^{\text{pc}} = \min(E^{\text{sil}}) = E_{H\#}^{\text{sil}} = 1000 \text{ K}$ and the barrier width $a_{H\#}^{\text{pc}}$ is 1 \AA and obtain $T_q \simeq 78 \text{ K}$ using eq. 8. Here we did not study the effects of different values for the barrier width. In addition, the shape of the barrier has been assumed to be rectangular although the use of most realistic barrier profiles may affect the results (Taquet et al. 2012). Knowing that $n_{\text{surf,chem}} = 4\pi N_{\text{surf}} r^2 n_d \simeq n_* + n_c$ (some chemisorbed sites can be occupied by D atoms), for T_d below 78 K , we can use the quantum tunnelling transfer function in the recombination-limited approximation ($E_{H\#}^{\text{sil}} \gg E_p^{\text{des}}$)

$$\alpha_{\text{pc}} \simeq v_{H\#}^{\text{pc}} \exp\left(-\frac{4\pi a_{H\#}^{\text{pc}}}{h} \sqrt{2m_H E_{H\#}^{\text{sil}}}\right) \text{ s}^{-1}. \quad (79)$$

For all $T_d < 78 \text{ K}$, $\alpha_{\text{pc}} \gg R_p^{\text{des}}$. The diffusion-chemisorption, i.e. when the rate coefficient is dominated by the chemisorption barrier term, for $T_d > 78 \text{ K}$ is

$$k_{H\#}^{\text{pc}} = v_{H\#}^{\text{pc}} e^{-E_{H\#}^{\text{pc}}/kT_d} / n_d n_{\text{site}} \text{ cm}^3 \text{ s}^{-1}. \quad (80)$$

The surface-mediated H_2 formation rate coefficient is in the thermal regime

$$k_{H\#, *H\#} \simeq v_{H\#, *H\#} e^{-E_{H\#, *H\#}/kT_d} / n_d n_{\text{site}} \text{ cm}^3 \text{ s}^{-1}. \quad (81)$$

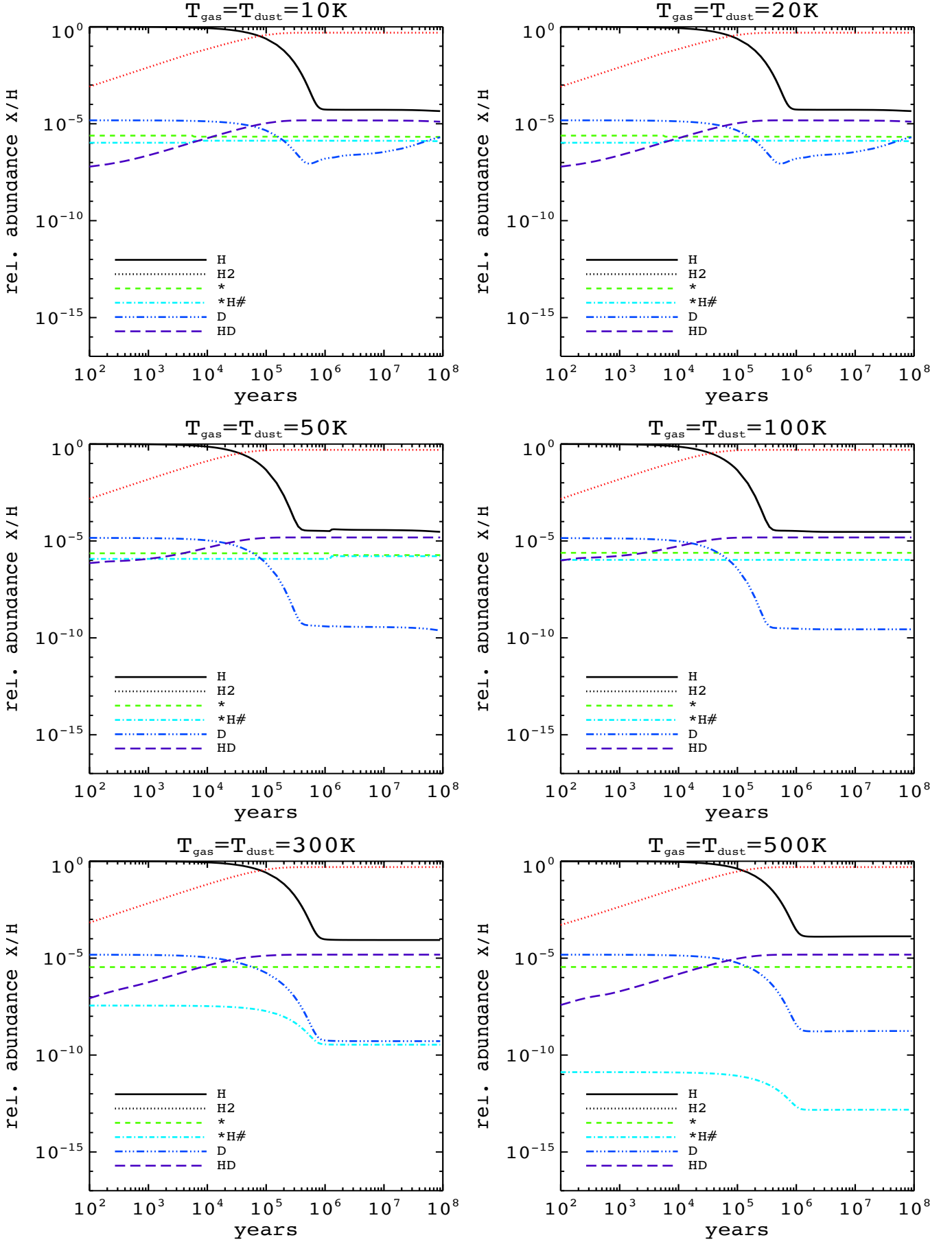


Fig. 3. H, H₂, D, HD, and physisorbed H as function of time using the surface chemistry model with physisorbed and chemisorbed species and a unique physisorption to chemisorption activation energy of 400 K. The first row are from left to right models at 10 and 20 K; the second row are models at 50 and 100 K. The bottom row shows models at 300 and 500 K. The * symbol corresponds to the abundance of unoccupied chemisorption sites.

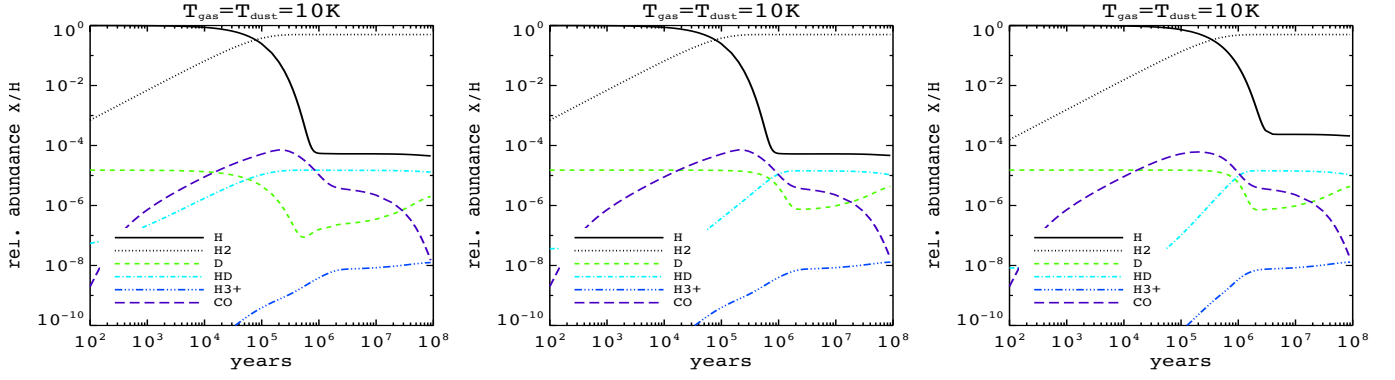


Fig. 4. H, H₂, D, HD, and physisorbed H as function of time at 10 K for three models of H₂ and HD formation. The left model is a surface chemistry model without chemisorption species; the middle panel is the model with the analytical Cazaux formation model and the right panel utilises the H₂ formation model of Jura (1974, 1975a,b).

The surface-mediated chemisorption processes rate becomes

$$\alpha_{pc} = k_{H\#}^{pc} n_{*} + k_{H\#,H\#} n_c \simeq \nu_{H\#}^{sil} e^{-E_{H\#}^{sil}/T_d} (n_{surf,chem}/n_d) / n_{b,site} s^{-1}, \quad (82)$$

which arranges to

$$\alpha_{pc} \simeq \nu_{H\#}^{sil} e^{-E_{H\#}^{sil}/kT_d} s^{-1}, \quad (83)$$

In the thermal regime,

$$\frac{R_p^{des}}{\alpha_{pc}} \simeq \frac{\nu_p^{des} e^{-E_p^{des}/kT_d}}{\nu_{H\#}^{sil} e^{-E_{H\#}^{sil}/kT_d}} \quad (84)$$

$$\frac{R_p^{des}}{\alpha_{pc}} \simeq \sqrt{\frac{E_p^{des}}{E_{H\#}^{sil}}} e^{-(E_p^{des} - E_{H\#}^{sil})/kT_d}. \quad (85)$$

In the diffusion-limited regime ($E_{H\#}^{sil} \ll E_p^{des}$), the ratio becomes

$$\frac{R_p^{des}}{\alpha_{pc}} \simeq \sqrt{\frac{E_p^{des}}{E_{H\#}^{diff}}} e^{-(E_p^{des} - E_{H\#}^{diff})/kT_d}. \quad (86)$$

The change of chemisorbed H-atom reads

$$dn_c/dt = k_{H\#}^{pc} n_p (n_{*} - n_c) - R_c^{des} n_c - 2k_{H_2}^{cc} n_c n_c. \quad (87)$$

In steady-state, the equation becomes

$$k_{H\#}^{pc} n_p (n_{surf,chem} - 2n_c) - R_c^{des} n_c - 2k_{H_2}^{cc} n_c n_c = 0, \quad (88)$$

which is a second degree equation in n_c . The solution is

$$n_c = 2\alpha_{pc} n_p / \left(-(R_c^{des} + 2k_{H\#}^{pc} n_p) + \sqrt{(R_c^{des} + 2k_{H\#}^{pc} n_p)^2 + 8k_{H_2}^{cc} \alpha_{pc} n_p} \right), \quad (89)$$

where $k_{H\#}^{pc} n_p n_{surf,chem} = \alpha_{pc} n_p$. If the desorption of chemisorbed H-atoms can be neglected

$$dn_{H_2}/dt \simeq \frac{1}{2} k_{H\#}^{pc} n_p n_{*}. \quad (90)$$

Since $n_p = R_H^{ads} n_H / (\alpha_{pc} + R_p^{des})$,

$$dn_{H_2}/dt \simeq \frac{1}{2} \left(1 + \frac{R_p^{des}}{\alpha_{pc}} \right)^{-1} R_H^{ads} n_H \quad (91)$$

The combination of equations 78, 89, and 5.1 can be divided by the H-atom impinging rate to give the H₂ formation efficiency for the Langmuir-Hinshelwood processes. The H₂ formation efficiency has been derived by (Cazaux & Tielens 2002, 2004) using a different model

$$\epsilon = \left(1 + \frac{R_p^{des}}{\alpha_{pc}} \right)^{-1} \xi, \quad (92)$$

with $R_p^{des} = \beta_{H_p}$, in Cazaux & Tielens (2002) and ξ the correction factor at high temperatures, which reflects the H atoms desorbing from chemisorption sites. Recent developments have shown that a layer of H₂ does not prevent the further formation of more H₂, thus we can neglect the first term in the parentheses in the formula of Cazaux & Tielens (2004). Both analytical efficiencies are shown in Fig. 2. Our curve has been obtained with a unique physisorption to chemisorption site activation energy of 400 K, which corresponds to a saddle point energy E_s of 200 K for the Cazaux's formula. Despite the differences in the treatment of many processes (presence of chemisorption sites, diffusion-mediated versus direct transfer from a physisorption site to an adjoining chemisorption site, "blocking" of chemisorption sites by ice layers, ...) between our model and the model from Cazaux & Tielens (2004), the agreement is remarkable for all temperatures apart in the upper end of the dust temperature range, i.e. when the efficiency drops faster than in the Cazaux's model due to the extra term $2k_{H\#}^{pc} n_p$ instead of only R_c^{des} when the efficiency is limited by the desorption only. As the efficiency remains relatively high even at 600 K, the actual H₂ formation rate is limited by the sticking coefficient at high dust temperatures (Cazaux et al. 2011). Part of the differences between the two efficiency curves can be ascribed to the use of different transmission function for α_{pc} (see Fig. E).

5.2. Numerical models of molecular clouds

The abundances of H, H₂, D, HD, H physisorbed and chemisorbed on grain surfaces are shown for the model for a zero-dimensional model at several temperatures (10, 20, 50, 100,

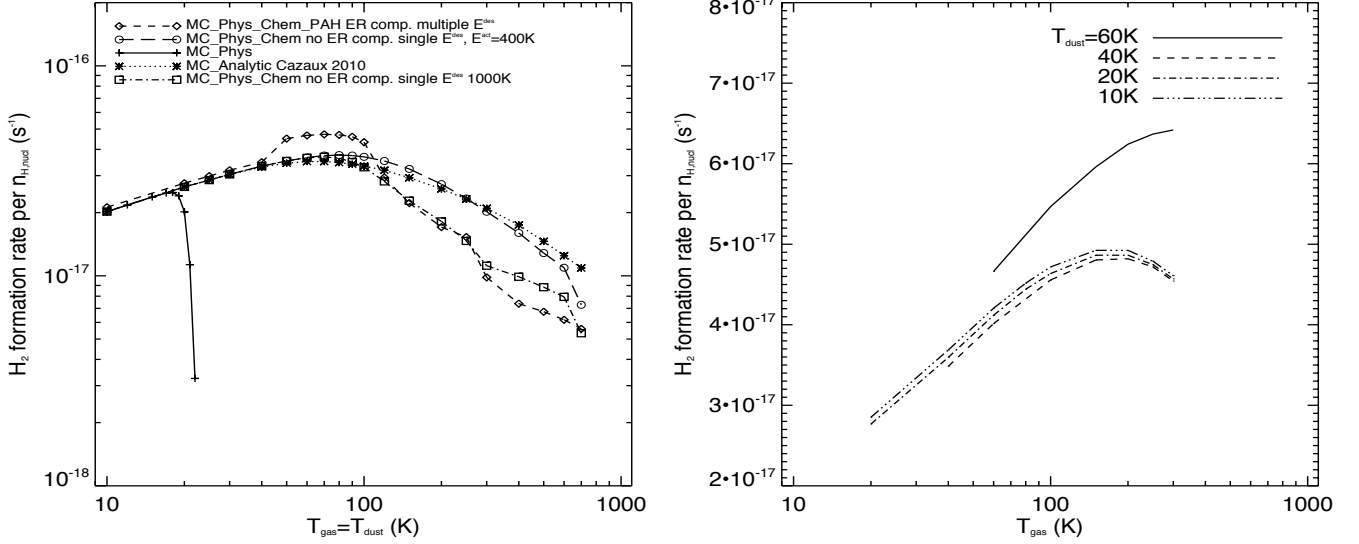


Fig. 5. Effective H₂ formation rate. The left panel shows two H₂ formation models for a molecular cloud of $n_{\text{H}} = 10^4 \text{ cm}^{-3}$ and assuming $T_{\text{d}} = T_{\text{g}}$ (MC-ANALYTIC, MC-PHYS and MC-PHYS-CHEM-PAH). We also show the effect of competition diffusion-reaction rates (no compet. MC-PHYS-CHEM-PAH). The right panel show H₂ formation model MC-PHYS-CHEM-PAH when T_{d} and T_{g} can be different.

300, and 500 K) with a single activation energy of 400 K from a physisorption to a chemisorption site at various grain temperatures in Fig. 3. The total conversion from H to H₂ is reached at all temperatures at $(1-2) \times 10^5$ yrs. The number density of atomic H plateaus at $\sim 1 \text{ cm}^{-3}$ after a few Myrs. At $T_{\text{d}} > 20 \text{ K}$, HD abundance reaches its maximum faster than H₂.

The abundance of surface hydrogen is predominately chemisorbed even at 10 K (see the top left panel of Fig. 3). Without chemisorption sites, the abundance of physisorbed H-atoms is 2.5 dex higher (see left panel of Fig. 4). This may affect the surface hydrogenation rates. The drop at time > 10 Myrs of the HD abundance is due to the strong fraction of HDO gas and HDO ice. The reason for this high chemisorption site occupancy is the large number of available chemisorption sites and the high surface diffusion rate.

We also run series of models with only physisorption sites, a model with an activation barrier for chemisorption of 1000 K instead of 400 K, and a model with multiple barrier height and Eley-Rideal formation processes included. The H₂ formation rate for a 0.1 micron grain is shown for the various models in the left panel of Fig. 5. The rates were computed from the outcomes of the models themselves by determining at each temperature the time t_{H_2} that the model needs to convert 2/3 of the hydrogen atoms to molecules, i.e. the time t_{H_2} such that $n_{\text{H}_2} = n_{\text{H}}$. The formation rate R is computed as $R = 1/(t_{\text{H}_2} n_{\text{H}})$.

Below 20 K, the H₂ formation is adsorption rate limited, independent on the actual H₂ formation rate on the grain surfaces as shown by the analytical treatment above. When the formation rate is low, the number density of H atom on the surface increases. This is the case when the rate is lower after the formation of H₂O ice layers. As expected, the desorption of H# above $\sim 20 \text{ K}$ prevents H₂ formation. The computed H₂ formation rate differences between the Cazaux model and the surface chemistry model with a single barrier for chemisorption corresponds to the differences seen in the analytical treatment (Fig. 2). H₂ formation is efficient up to $\sim 700 \text{ K}$ (efficiency of 0.4), which corresponds to $\sim E_{\text{c}}^{\text{des}}/30$ (Luna et al. 2017). Atomic D is only slightly more bound to the surface and will also form efficiently

on grains up to $\sim 700 \text{ K}$. The building up of ice layers does not prevent surface H-atoms to reach the silicate surface and to adsorb on an empty chemisorption site. Both the diffusion and desorption rates decrease with increasing number of ice layers.

The model with a single barrier of 1000 K for chemisorption shows a drop in efficiency above 100 K. It reflects the decrease in the $R_{\text{p}}^{\text{des}}/\alpha_{\text{pc}}$ ratio with a higher energy barrier. In the model with varying barrier energy and chemisorption desorption energy, the efficiency is similar to the model with a single barrier at 1000 K. The higher H₂ formation rate is due to the H₂ formation by the Eley-Rideal mechanism, whose rate can be as high as the Langmuir-Hinshelwood rate (Le Boulart et al. 2012). H₂ formation through single hydrogenated PAHs and cation PAHs is less efficient at all temperatures than on silicate grains because the rate is basically an Eley-Rideal mechanism rate. The models assume that only atomic H and D can chemisorb. In more realistic models where the chemisorption sites can be occupied by other species (e.g., -OH), the efficiency of H₂ formation on silicate grains may decrease and the fraction of H₂ formed via hydrogenated PAHs increases. The H₂ formation rate by H-atom abstraction of hydrogenated PAHs will increase if we adopt a larger abstraction cross-section (see appendix C). Studies have suggested that cross-sections more than ten times higher than our value may be possible (Zecho et al. 2002). The additional path to form H₂ through the hydrogenated PAHs is required to explain observed H₂ formation rates that are higher than the theoretical limit set by the H atom impinging rate on grain surfaces. In this study, we have not included H₂ formation via photodissociation of Hydrogenated Amorphous Carbon nano-grains (HACs). Jones & Habart (2015) examined this route and concluded that this mechanism could be efficient for warm grains ($T=50-100 \text{ K}$) in moderately UV-illuminated regions ($I_{\text{UV}}=1-100$). Duley & Williams (1993) has described a model of H₂ formation on carbonaceous grains at temperatures found in protoplanetary disks. The H₂ formation on HACs would be explored in future studies.

In Fig. 4 we compare the abundances of the standard model with models without chemisorbed species, the analytical Cazaux

model and the Jura model (Jura 1974, 1975a,b). As expected the H_2 formation rates in the full surface chemistry and in the analytical model are quasi-identical. HD formation rate in the Cazaux model is slower than in the other models.

On the right panel of Fig. 2 the effects of different gas and dust temperatures are shown for dust grain temperatures between 10 and 60 K for models that include the Langmuir-Hinshelwood and Eley-Rideal H_2 formation mechanism. The ER H_2 formation is efficient for warm gas and dust consistent with Le Bourlot et al. (2012). However, the efficiency drops for dust grains above 100 K when the desorption of physisorbed H-atoms start to overtake the transfer of the atom to a chemisorption site compared to the H_2 formation by the encounter between a physisorbed and a chemisorbed atom. The H_2 formation rate increases with grain surface temperature as expected, although just by a factor 2. This enhancement compared to the standard value may be insufficient to explain observations of abundant hot H_2 gas (Habart et al. 2004).

Our conclusions may change in the future because our results depend critically on numerous rates that are difficult to measure or compute.

6. Conclusions & perspectives

We have implemented a detailed H_2 and HD formation model in the ProDiMo code. The model extends the rate-equation treatment of surface reactions to chemisorbed species assuming diffusion-reaction competition surface rates. We modeled the Langmuir-Hinshelwood and Eley-Rideal mechanisms for physisorbed and chemisorbed H and D atoms. We introduced the concept of chemisorption sites as a pseudo-species, which facilitates the computation of chemisorbed species. We also accounted for the formation of H_2 and HD on hydrogenated PAH and PAH cations. We implemented a charge exchange chemistry between the PAHs and the other gas-phase species. The Langmuir-Hinshelwood processes (between two physisorbed H-atoms, between a physisorbed and a chemisorbed atom, and between two chemisorbed atoms) are the main H_2 formation route at all dust temperatures. H_2 also form efficiently by the Eley-Rideal mechanism between 50 and 100 K. The contribution of singly and multiply-hydrogenated PAHs and PAH ions to the H_2 formation is limited when a small cross-section for hydrogen abstraction is adopted. The value of the cross-section varies by orders of magnitude from study to study. More experimental and theoretical works are warranted before a more definitive conclusion on the importance of H_2 formation through hydrogenated PAHs can be drawn. HD formation proceeds both on the grain surfaces and in the gas-phase. For all dust temperatures below the chemisorption desorption temperature in the case of low photodesorption, the surface-mediated chemisorption processes dominate over the desorption of physisorbed H-atoms. Our implementation of a warm surface chemistry can be used to model H_2 and HD formation in Photodissociation Regions, protoplanetary disks, and other astrophysical environments where the dust temperature is above 20 K. Future study will include the formation of H_2 on carbonaceous grain surfaces.

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can help us understand the behaviour of the sticking coefficient as function of the parameters such as gas and dust temperature as well as the binding energy.

The Goodman’s version of the modified Baule formula gives the transfer of energy between the incident particle and the surface accounting for surface at temperature T_d (Bonfanti & Martinazzo 2016)

$$\delta\epsilon = 2.4 \frac{\alpha}{(1 + \alpha)^2} \left(\epsilon + D - \frac{1}{2} k T_d \right), \quad (\text{A.1})$$

where α is the mass ratio between the incident species of mass m_i to the surface mass m_{surf} , ϵ is the kinetic energy of the incident species at temperature T_g ($\epsilon = 1/2 k T_g$), E_i^b is the binding energy, the surface is at temperature T_d . $D = 3/4 E_i^b$ as suggested by Hollenbach & Salpeter (1970). The original Baule formula uses a pre-factor of 4 instead of 2.4. When $\epsilon + D - \frac{1}{2} k T_d < 0$, the species returns to the gas-phase with extra energy acquired from the surface. Alternatively, one can use the formula in Hollenbach & Salpeter (1970) modified to account for the dust surface temperature. First we define a characteristic frequency of the repulsive collision

$$\omega_0 = [(\epsilon + D - 0.5 k T_d) / 2 m_i b^2]^{1/2}, \quad (\text{A.2})$$

where b is the experimental determined slope parameter with a value $b = 0.30 \text{ \AA}$ from (Hollenbach & Salpeter 1970). When $1 \lesssim \omega/\omega_0 \lesssim 1.68$

$$\delta\epsilon = \alpha \left(\epsilon + D - \frac{1}{2} k T_d \right), \quad (\text{A.3})$$

where ω is the Debye frequency of the solid $k \theta_D = \hbar \omega / 2\pi$, where θ_D is the Debye temperature in Kelvin. For crystalline water ice, we use $\theta_D = 222.2 \text{ K}$ (Flubacher et al. 1960), which gives $\omega = 2.9 \times 10^{13} \text{ s}^{-1}$ compared to $\omega_0 = 4 \times 10^{13} \text{ s}^{-1}$ at 78 K (Hollenbach & Salpeter 1970). The Debye temperature for crystalline olivine is 753 K (Chung 1971). When $\omega/\omega_0 \gtrsim 1.68$

$$\delta\epsilon = \alpha \left(\epsilon + D - \frac{1}{2} k T_d \right) 2 [\omega_0^2 / (\omega^2 - \omega_0^2)]. \quad (\text{A.4})$$

The sticking coefficient is within about 5% Hollenbach & Salpeter (1970)

$$S \approx \frac{\gamma^2 + 0.8 \gamma^3}{1 + 2.4 \gamma + \gamma^2 + 0.8 \gamma^3}, \quad (\text{A.5})$$

where $\gamma \equiv E_i^c / k T_g$, $E_i^c = \Omega (D \delta\epsilon)^{1/2}$. Ω is a factor that accounts for the type of surface rebonds: $\Omega^2 \simeq 1$ for Lambert’s law and $\Omega^2 = 2$ for isotropic scattering above the surface (Hollenbach & Salpeter 1970). We chose $\Omega^2 = 2$, consistent with a rough surface. The sticking coefficient reduces to $S \simeq \gamma^2$ for $\gamma \ll 1$ (inefficient energy transfer) and to $S \simeq 1 - 3/\gamma^2$ for $\gamma \gg 1$ (efficient energy transfer). The sticking coefficient increases with the binding energy. Hollenbach & Salpeter (1970) used a value $\delta\epsilon = 17 \text{ K}$ for H collision with water ice.

Appendix A: Sticking coefficient

Although the sticking coefficient can modify the H_2 (HD) formation rate, it does not effect the efficiency of the surface recombination. We discuss here a simple qualitative model, whose

Appendix B: PAH charge exchange chemistry

A model of PAH ionization has been presented by Dartois & D’Hendecourt (1997). We used the circumcoronene ($\text{C}_{54}\text{H}_{18}$) as typical PAHs that are large enough to escape photodissociation

Table B.1. Circumcoronene electron affinity and ionisation potential. The measured (lit.) and computed (WD2001) values are shown.

	E.A. (eV)	I.P. (eV) lit.	I.P. WD2001
$C_{54}H_{18}$	1.3	5.9	6.2
$C_{54}H_{18}^+$...	8.8	9.4
$C_{54}H_{18}^{2+}$...	12.9	12.5

in disks around HerbigAe stars. The circumcoronene can be once negatively-charged (PAH^-) and three times positively charged by absorbing a UV with energy below 13.6 eV or by charge exchange reactions (PAH^+ , PAH^{2+} , PAH^{3+} , see Table B.1). The effective radius of a PAH is computed by (Weingartner & Draine 2001)

$$a_{PAH} = 10^{-7} \left(\frac{N_C}{468} \right)^{1/3} \text{ cm}, \quad (B.1)$$

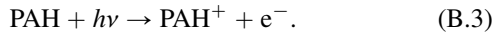
where N_C is the number of carbon atoms in the PAH. The radius for the circumcoronene is $a_{PAH}(C_{54}H_{18}) = 4.686 \times 10^{-8}$ cm. The PAH ionisation potential can either be taken from the literature when they are measured or estimated (Weingartner & Draine 2001)

$$IP_{PAH} = W_0 + (Z_{PAH} + 0.5) \frac{e^2}{a_{PAH}} + (Z_{PAH} + 2) \frac{e^2}{a_{PAH}} \frac{0.3 \times 10^{-8}}{a_{PAH}} \text{ erg}, \quad (B.2)$$

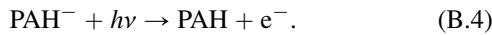
where W_0 is the work function assumed to be 4.4 eV (7.05×10^{-12} erg), and Z_{PAH} is the charge of the PAH. The ionisation potentials (I.P.) are listed in Table B.1.

B.1. PAH photoionisation and PAH^- photodetachment

Stellar and interstellar ultraviolet photons with energy below 13.6 eV ionise neutral and ionised PAHs in disk surfaces



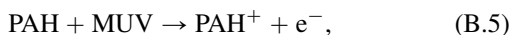
The photoionisation rates at each disk location were computed by integrating the product of the photoionisation cross-sections calculated using the PAH model of Li & Draine (2001) with the internal UV field obtained by solving the continuum dust radiative transfer and a yield computed according to the prescription of Jochims et al. (1996). PAH self-shielding is taken into account. PAH^- can lose its electron by absorbing a stellar or interstellar UV photon (photodetachment):



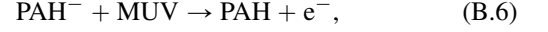
The rates are computed the same way as for the photonionisation.

B.1.1. Energetic particles induced photoionisation and photodetachment

H_2 collisionally excited to Rydberg states by fast 'secondary' electrons generated by energetic particles (cosmic ray, X-ray, or radioactive decay) ionisation of hydrogen fluoresces in the ultraviolet. The fluorescence photons have enough energies to ionise an electron from a PAH



or detach an electron from a PAH anion



where MUV stands for UV generated by gas interaction with MeV particles. The number of fluorescence photons with energies between 7.1 and 14.6 eV is $f_{Ryd}\zeta n_H$ (Flower & Pineau des Forêts 2003), where f_{Ryd} is the fraction of the secondary electrons that excite the H_2 , ζ is the rate (s^{-1}) of total hydrogen ionisation (cosmic ray, X-ray, and radioactive decay). We adopted a value of 0.15 for f_{Ryd} (Flower & Pineau des Forêts 2003). The rate coefficient for photoionisation triggered by energetic events is

$$k_{pi,MeV} = 0.15\zeta n_H g_{PAH} y_{pi} \text{ cm}^{-3} \text{ s}^{-1} \text{ cm}^3 \text{ s}^{-1}, \quad (B.7)$$

where g_{PAH} is the fraction of the photons absorbed by the neutral or positive PAHs compared to the total opacity and y_{pi} is the yield of photodetachment. Likewise, the rate coefficient for photodetachment is

$$k_{pd,CR} = 0.15\zeta n_H g_{PAH^-} y_{pd} \text{ cm}^{-3} \text{ s}^{-1}, \quad (B.8)$$

where g_{PAH^-} the fraction of the photons absorbed by the negative PAHs and y_{pd} is the yield of photodetachment. The reactions may be important in the UV-shielded environments

Table B.2. PAH cation recombination rate coefficients measured at room temperature (300 K) by Biennier et al. (2006). Alternative values are also listed in the bottom of the table.

Name	Formula	k [$\text{cm}^3 \text{ s}^{-1}$]	Ref.
naphtalene	$C_{10}H_8^+$	$0.3(\pm 0.1) \times 10^{-6}$	<i>a</i>
azulene	$C_{10}H_8^+$	$1.1(\pm 0.1) \times 10^{-6}$	"
acenaphtalene	$C_{12}H_{10}^+$	$0.5(\pm 0.2) \times 10^{-6}$	"
anthracene	$C_{14}H_{10}^+$	$2.4(\pm 0.8) \times 10^{-6}$	"
phenanthrene	$C_{14}H_{10}^+$	$1.7(\pm 0.5) \times 10^{-6}$	"
fluoranthene	$C_{16}H_{10}^+$	$3.0(\pm 0.9) \times 10^{-6}$	"
pyrene	$C_{16}H_{10}^+$	$4.1(\pm 1.2) \times 10^{-6}$	"
naphtalene	$C_{10}H_8^+$	$0.3(\pm 0.1) \times 10^{-6}$	<i>b</i>
anthracene	$C_{14}H_{10}^+$	$1.1(\pm 0.5) \times 10^{-6}$	<i>c</i>

Notes. ^aBiennier et al. (2006); ^bAbouelaziz et al. (1993); ^cNovotny et al. (2005)

B.1.2. Electron recombination

Ionised PAHs can recombine with electrons. The electron recombination rate with singly-ionised PAHs



are calculated following a classical formalism by assuming that PAH-cations and electrons interact via a Coulomb potential (Bakes & Tielens 1994; Tielens 2005):

$$k_{er} = 4.1 \times 10^{-5} \phi_{PAH} f(a_{PAH}) \left(\frac{N_C}{50} \right)^{1/2} \left(\frac{100K}{T_g} \right)^{1/2} \text{ cm}^3 \text{ s}^{-1}, \quad (B.10)$$

where N_C is the number of carbon atoms and ϕ_{PAH} a correction factor for the disk shape: $\phi_{PAH} = \sigma_{disk}/\sigma_{sphere}$ between 0.1 and 0.8 (Verstraete et al. 1990). The recombination is essentially not dissociative for the large PAHs present in disks. An experimental study of the recombination of PAH cations with electron has

been performed by Biennier et al. (2006) at room temperature for seven small PAH cations. For multiply-ionised PAHs, the recombination rate is enhanced

$$k'_{\text{er}} = k_{\text{er}} \times \left(1 + \frac{W_{\text{PAH}}}{kT_{\text{elec}}}\right), \quad (\text{B.11})$$

where the $W_{\text{PAH}} = IP_{\text{PAH}}(Z_{\text{PAH}}) - IP_{\text{PAH}}(0)$ is the work function and is equal to the difference in ionisation potential between the charged and neutral PAH. If no experimental results exist and we assumed $T_{\text{elec}} = T$. We assumed that the recombination of PAH-H^+ cations are dissociative and have the same rates as for PAH cations. For PAH with fewer than 20 carbon atoms, an additional correction factor has to be applied to match the experimental data

$$f(a_{\text{PAH}}) = (1 - \exp(-12 \times a_{\text{PAH}}/l_{e-})) / (1.0 + \exp(12 - N_C)), \quad (\text{B.12})$$

where a_{PAH} is the PAH radius in cm and $l_{e-} = 10^{-7}$ cm (Weingartner & Draine 2001). Alternatively, Flower & Pineau des Forêts (2003) adopted a size-independent rate

$$k_{\text{er}} = 3.3 \times 10^{-6} \left(\frac{300\text{K}}{T}\right)^{1/2} \text{ cm}^3 \text{ s}^{-1}. \quad (\text{B.13})$$

Both rates can be reconciled if we take $\phi_{\text{PAH}} \simeq 0.2$. For PAHs with 10 carbon atoms or fewer, the recombinations are dissociative (Abouelaziz et al. 1993; Fournier et al. 2013). The comparison between the adopted rates and the laboratory data for singly-ionised PAH cations is shown in Fig. B.1. The derived re-

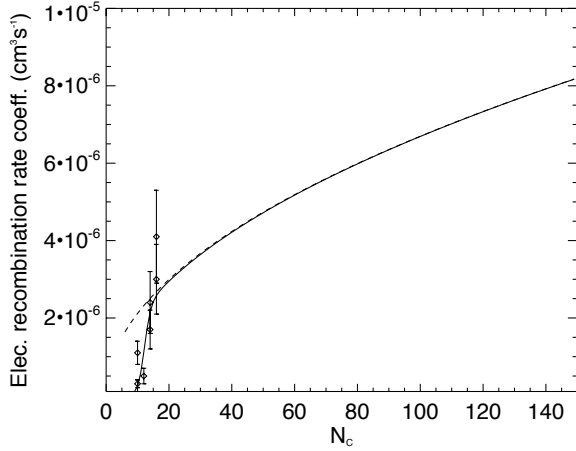


Fig. B.1. PAH^+ cation electron recombination rate coefficient as function of the number of carbon atoms using equation B.10 assuming $\phi_{\text{PAH}} = 0.2$ and $T = 300$ K (dash-line). The experimental data from Biennier et al. (2006) are listed in Table B.2. The solid line includes the additional correction $f(a_{\text{PAH}})$ for PAHs of radius a_{PAH} applied to the adopted law to match the experimental data.

combination rates assuming $\phi_{\text{PAH}} \simeq 0.4$ for circumcoronene are given in Table B.3. The rate coefficients as function of the gas temperature are shown in Fig. B.2.

B.1.3. Electron attachment

Electrons can attach on neutral PAHs. Experiments have shown that the electron attachment cross section is a strong function of

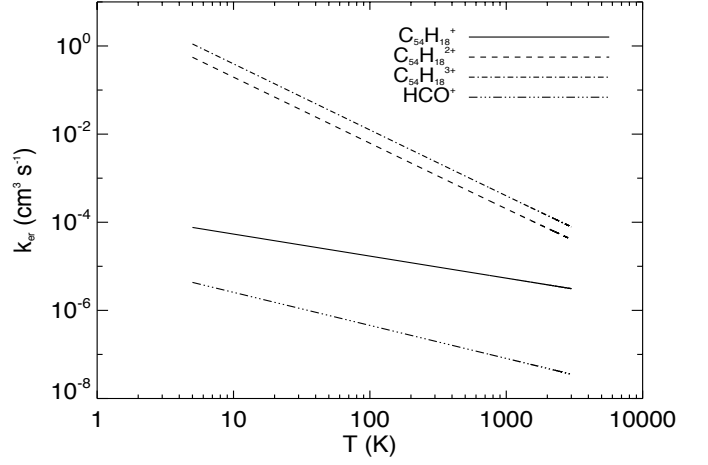


Fig. B.2. Electron recombination rate coefficients for the PAH cations.

Table B.3. Circumcoronene cation electron recombination rate coefficients ($\phi_{\text{PAH}} = 0.4$). By comparison the recombination rate coefficient for HCO^+ is also shown.

Formula	k [$\text{cm}^3 \text{ s}^{-1}$]
$\text{C}_{54}\text{H}_{18}^+$	$1.7 \times 10^{-5} \left(\frac{100\text{K}}{T}\right)^{1/2}$
$\text{C}_{54}\text{H}_{18}^{++}$	$1.7 \times 10^{-5} \left(\frac{100\text{K}}{T}\right)^{1/2} \left(1 + \frac{36438.8}{T}\right)$
$\text{C}_{54}\text{H}_{18}^{+++}$	$1.7 \times 10^{-5} \left(\frac{100\text{K}}{T}\right)^{1/2} \left(1 + \frac{72877.6}{T}\right)$
HCO^+	$3.0 \pm 0.9 \times 10^{-7} \left(\frac{T}{300\text{K}}\right)^{-0.74 \pm 0.02}$

the electron affinity (Tobita 1992), which changes the electron sticking coefficient $S_{\text{PAH}}(e^-)$. The electron attachment rates can be written as (Allamandola et al. 1989)

$$k_{\text{ea}} = S_{\text{PAH}}(e^-) k_f \text{ cm}^3 \text{ s}^{-1}, \quad (\text{B.14})$$

where k_f is the electron capture rate. We adopt the sticking coefficient analytical formula from Weingartner & Draine (2001)

$$S_{\text{PAH}}(e^-) = (1 - e^{-a_{\text{PAH}}/l_{e-}}) / (1 + e^{(20 - N_C)}), \quad (\text{B.15})$$

where a_{PAH} is the radius of the PAH in cm and l_{e-} is the electron escape length equal to 10^{-7} cm (see Fig. B.3). The capture rate follows a Langevin law and thus does not depend on the temperature:

$$k_f = 8.5 \times 10^{-7} \phi_{\text{PAH}} \sqrt{N_C}. \quad (\text{B.16})$$

Large PAHs ($N_C > 20$) have electron affinity large enough (~ 1 eV) such that the electron sticking coefficient on PAHs $S(e^-)$ is close to unity. The electron attachment rates are approximated by

$$k_{\text{ea}} = 8.5 \times 10^{-7} S_{\text{PAH}}(e^-) \phi_{\text{PAH}} \left(\frac{N_C}{50}\right)^{1/2} \text{ cm}^3 \text{ s}^{-1}. \quad (\text{B.17})$$

The rates are high compared to atomic electronic attachment rate coefficients, whose values are 10^{-16} – 10^{-14} $\text{cm}^3 \text{ s}^{-1}$. The electron attachment rate as function of the number of carbon N_C is displayed in Fig. B.4. The formula is consistent with the measured value of 10^{-9} $\text{cm}^3 \text{ s}^{-1}$ for anthracene ($\text{C}_{14}\text{H}_{10}$) by Canosa et al. (1994). Other measurements by Moustefaoui et al. (1998) show that the rates are temperature independent and lie between 1 and 3×10^{-9} $\text{cm}^3 \text{ s}^{-1}$ for anthracene, consistent with

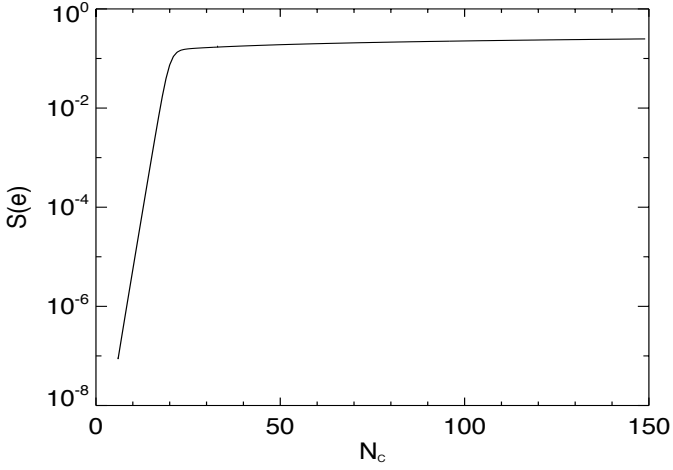


Fig. B.3. PAH electron sticking coefficient.

our choice. For $N_c=30$, our rate is 10 times smaller than in other studies because they adopt a $N_c^{3/4}$ variation (Wakelam & Herbst 2008; Omont 1986).

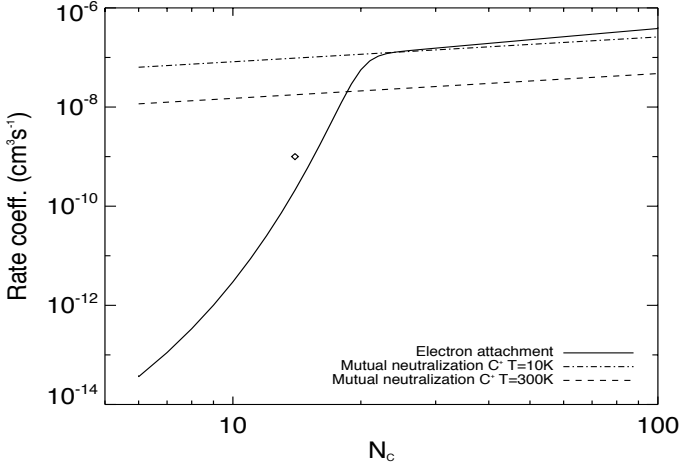
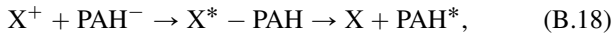


Fig. B.4. PAH rate coefficients. The solid line is the electron attachment rate coefficients. The diamond is the measured PAH attachment rate coefficient for anthracene (Canosa et al. 1994). The dashed- and dashed-dotted lines are the mutual neutralisation rates C^+ at two kinetic temperature.

B.1.4. PAH mutual neutralisation reactions

The mutual neutralisation reactions between any atomic cation X^+ and PAH



where X^* and PAH^* are excited intermediate species, proceeds at the rate

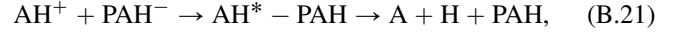
$$k_{mn} = 2.9 \times 10^{-7} \phi_{PAH} \left(\frac{12 \text{ amu}}{m_X} \right)^{1/2} \left(\frac{100K}{T} \right)^{1/2} \left(\frac{N_c}{50} \right)^{1/2} \text{ cm}^3 \text{ s}^{-1}, \quad (B.19)$$

where m_X is the mass of species X and amu is the value of the atomic mass units. An alternative parametrisation has been proposed to match experimental mutual neutralisation of simple and

clustered positive and negative ions (Hickman 1979)

$$k_{mn} = 5.33 \times 10^{-7} (T/300)^{-0.5} \mu^{-0.5} (E.A.)^{-0.4} \text{ cm}^3 \text{ s}^{-1}, \quad (B.20)$$

where the reduced mass μ of the ion pair is in atomic mass units and the electron affinity $E.A.$ (electron detachment energy of the negative ion) is in eV. The latter formula has been shown to be quite successful in fitting laboratory data (Miller 1980; Smith, Church, & Miller 1978). For HCO^+ , $\mu \simeq 29 \text{ amu}$. The electron affinity is $\sim 1 \text{ eV}$ for large PAHs. The temperature-dependence is the same for the two parameterisations. For a molecular cation AH^+ the mutual neutralisation can be dissociative:



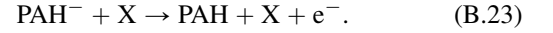
or not



The branching ratio between the two modes is unknown. In the gas phase, electronic recombinations are dissociative because the ionisation potentials are higher than the A-H bond energy. In the case of the recombination with negatively-charged PAHs the excess energy can be transferred to the PAHs, which have enough vibrational modes to decay rapidly. In this work, both branches are assumed to have the same probability (0.5). All atomic and molecular ions react with PAH^- and we adopt the first parametrisation. The rate at 10 and 300 K for a carbon ions and with $\phi_{PAH} = 0.2$ is shown in Fig. B.4.

B.1.5. PAH collisional detachment reactions

Neutral species can detach the electron from negatively-charged PAHs



The rate follows the prescription of Flower & Pineau des Forêts (2003)

$$k_{nd} = 1.5 \times 10^{-8} \phi_{PAH} \left(\frac{1 \text{ amu}}{m_X} \right)^{1/2} \left(\frac{N_c}{50} \right)^{1/2} e^{-5500/T} \text{ cm}^3 \text{ s}^{-1}, \quad (B.24)$$

with $\phi_{PAH}=0.2$. The activation barrier is $E_a/k=5500 \text{ K}$. Therefore PAH will be more neutralised by this process in hot disk mid-planes.

B.1.6. PAH charge exchange reactions

Neutral and positively-charged PAHs can undergo charge exchanges with ions.



where $n \geq 0$. The criterium for the reaction to proceed is that the reaction is energetically allowed, i.e. the ionisation potential (I.P.) of species X is higher than that of PAH^{n+} . Flower & Pineau des Forêts (2003) adopted a reaction probability of 0.1 per collision for reactions with $n = 0$. We adopt the rate coefficients from Tielens (2005) for $n = 0$:

$$k_{ce,0} = 2.9 \times 10^{-8} \phi_{PAH} \left(\frac{1 \text{ amu}}{m_X} \right)^{1/2} \left(\frac{100K}{T} \right)^{1/2} \left(\frac{N_c}{50} \right)^{1/2} \text{ cm}^3 \text{ s}^{-1}, \quad (B.26)$$

and

$$k_{ce,n} = k_{ce,0} \times \max \left(0, 1 - \frac{ne^2}{a_{PAH} k T} \right) \text{ cm}^3 \text{ s}^{-1}, \quad (B.27)$$

for positively-charged PAHs ($n > 0$) where the effect of the repulsive potential between the two positively-charged species is taken into account. Assuming that the PAH is a circumcoronene, the minimum temperature required to overcome the repulsion is

$$T_{\min} > \frac{e^2}{a_{\text{PAH}}k} = 16710 \left(\frac{N_C}{468} \right)^{-1/3} \text{ K.} \quad (\text{B.28})$$

For circumcoronene, there is no realistic gas temperature for which the rate $k_{\text{ce},n>0}$ is not null. Alternatively one can use

$$k_{\text{ce},n} = k_{\text{ce},0} \times \max \left(0, 1 - \frac{W_{\text{PAH}}}{kT} \right) \text{ cm}^3 \text{ s}^{-1}. \quad (\text{B.29})$$

For singly- positively-charge PAH circumcoronene $W_{\text{PAH}} = 2.9$ eV or 33 652.9 K. Both formulations show that only large singly-charged PAHs can exchange charge with cations at high gas temperatures. In protoplanetary disk conditions, those reactions do not occur.

Tielens (2005) also considers a double electron transfer from He^+ to neutral PAHs because of the high value of the helium ionization potential:



with the rate

$$k_{\text{di}} = 1.1 \times 10^{-8} \phi_{\text{PAH}} \left(\frac{N_C}{50} \right)^{1/2} \text{ cm}^3 \text{ s}^{-1}. \quad (\text{B.31})$$

Inversely, positively-charged PAHs can gain an electron from ions



Among the major atomic and molecular species, only sodium (Na) has an I.P. that is lower than that of the adopted PAH.

B.2. PAH adsorption on grain surfaces

In addition to the hydrogenation, neutral PAHs can be ionised or condense (physisorption) onto grain surfaces with an adsorption energy that scales with the number of hydrogen and carbon atoms (Kamp et al. 2017):

$$E_{\text{PAH,des}}/k = 482 \times (N_C - N_H) + 946 \times N_H \text{ K}, \quad (\text{B.33})$$

where E_{CC} ($= 482$ K) is the fitted desorption energy per graphene-like carbon ($N_{\text{CC}} = N_C - N_H$), and E_{CH} ($= 946$ K) is the fitted energy per benzene-like carbon and its adjoining H-atom ($N_{\text{CH}}=N_H$). Graphenes are completely de-hydrogenated PAHs. Graphene-like carbons are C-atoms with three covalent bonds with carbons, whereas benzene-like carbon have two covalent bonds with carbons and one bond with a hydrogen atom. For circumcoronene ($N_{\text{CC}}=36$ and $N_{\text{CH}}=18$), the estimated desorption energy is 34380 K. The highest possible value is set by the heat of vaporisation for graphite at $H_f/k = 86240$ K (Pierson 1993). Michoulier et al. (2018) have calculated the binding energy of PAHs on water ice. For coronene, they found binding energies between 20330 and 28140 K, compared to a value of 17136 K derived using our formula. For simplification, we chose to use the same adsorption energy whatever the type of surface.

Appendix C: Multi-hydrogenated PAHs

We ran three series of molecular cloud models with physisorption only and H_2 formation on multi-hydrogenated PAHs (up to PAH-H_{18}) and without deuterium chemistry. One series of models was run with a standard hydrogen abstraction cross-section of $\sigma=0.06 \text{ \AA}^2$ and the other series with a tenfold cross-section ($\sigma=0.6 \text{ \AA}^2$) and hundredfold cross-section ($\sigma=6 \text{ \AA}^2$). Figure C.1 shows that unless a large cross-section is assumed, the H_2 formation through hydrogenated PAHs is not as efficient as via chemisorbed H atoms at temperatures greater than 100 K. The H_2 formation rate with large cross-sections are higher than on silicate grain surfaces for temperatures greater than 200 K. The high H_2 formation rate below 20 K is due to the formation from physisorbed H-atoms on (icy) silicate grains. The asymptotic theoretical maximum H_2 formation rate can be estimated by

$$R_{\text{PAH-H}_x,\text{max}} = \sigma(kT_g/(2\pi m_H))^{1/2}(n_{\text{PAH}}/n_H)\bar{x}, \quad (\text{C.1})$$

where $\chi_{\text{PAH}} = n_{\text{PAH}}/n_H$ is the PAH abundance and \bar{x} the average hydrogenation state of the PAHs. Introducing the numerical values, the maximum rate becomes

$$R_{\text{PAH-H}_x,\text{max}} \simeq 10^{-16} f_{\text{PAH}} \left(\frac{\sigma}{10 \text{ \AA}^2} \right) \left(\frac{T_g}{100 \text{ K}} \right)^{1/2} \left(\frac{\bar{x}}{10} \right) \text{ s}^{-1}. \quad (\text{C.2})$$

We plotted the theoretical maximum H_2 formation rate using this formula with $f_{\text{PAH}} = 1$, $x = 18$, and $\sigma = 6 \text{ \AA}^2$ in Fig. C.1.

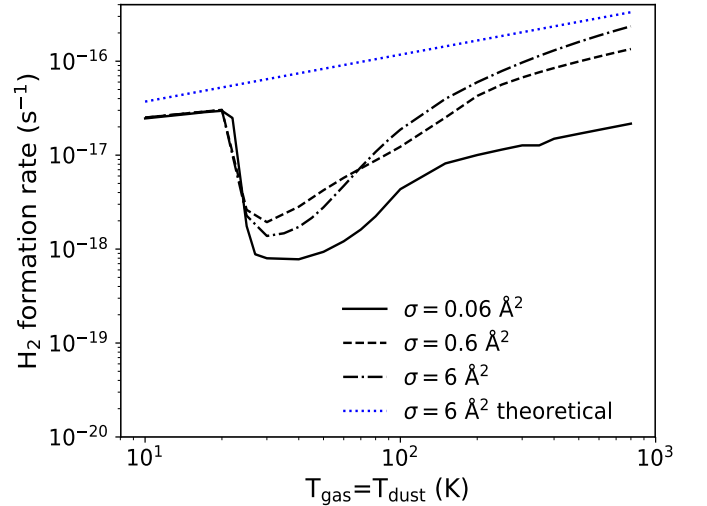


Fig. C.1. H_2 formation rate with adsorbed H on grains and multi-hydrogenated PAHs (up to PAH-H_{18}). The two series show the effect of assuming the abstraction cross-section from Mennella et al. (2012) and when assuming a tenfold cross-section.

Appendix D: Chemical network

The species modeled in this study are shown in Table D.1.

Table D.1. Gas and solid species in the network.

12 elements	H, He, C, N, O, Ne, Na, Mg, Si, S, Ar, Fe	
(H)	H, H ⁺ , H ⁻ , H₂ , H ₂ ⁺ , H ₃ ⁺ , H ₂ ^{exc}	7
(He)	He, He ⁺ ,	2
(C-H)	C, C ⁺ , C ⁺⁺ , CH, CH ⁺ , CH₂ , CH ₂ ⁺ , CH ₃ , CH ₃ ⁺ , CH₄ , CH ₄ ⁺ , CH ₅ ⁺ ,	12
(C-N)	CN, CN ⁺ , HCN , HCN ⁺ , HCNH ⁺	5
(C-O)	CO , CO ⁺ , HCO, HCO ⁺ , CO₂ , CO ₂ ⁺ , HCO ₂ ⁺ ,	7
(N-H)	N, N ⁺ , N ⁺⁺ , NH, NH ⁺ , NH ₂ , NH ₂ ⁺ , NH₃ , NH ₃ ⁺ , NH ₄ ⁺	9
(N-N)	N ₂ , N ₂ ⁺ , HN ₂ ⁺ ,	3
(N-O)	NO, NO ⁺ ,	2
(O-H)	O, O ⁺ , O ⁺⁺ , OH, OH ⁺ , H₂O , H ₂ O ⁺ , H ₃ O ⁺ ,	8
(O-O)	O₂ , O ₂ ⁺ ,	2
(O-S)	SO, SO ⁺ , SO₂ , SO ₂ ⁺ , HSO ₂ ⁺	5
(S-H)	S, S ⁺ , S ⁺⁺ ,	3
(Si-H)	Si, Si ⁺ , Si ⁺⁺ , SiH, SiH ⁺ , SiH ₂ ⁺ ,	6
(Si-O)	SiO , SiO ⁺ , SiOH ⁺ ,	3
(Na)	Na, Na ⁺ , Na ⁺⁺ ,	3
(Mg)	Mg, Mg ⁺ , Mg ⁺⁺ ,	3
(Fe)	Fe, Fe ⁺ , Fe ⁺⁺ ,	3
(Ne)	Ne, Ne ⁺ , Ne ⁺⁺ ,	3
(Ar)	Ar, Ar ⁺ , Ar ⁺⁺ ,	3
ice	CO#, H ₂ O#, CO ₂ #, CH ₄ #, NH ₃ #, SiO#, SO ₂ #, O ₂ #, HCN#, N ₂ #,	10
additional elements	PAH, *	2
additional species	H#, H ₂ #, *H#, D, D+, D-, HD, D#, HD#, *D#, H ₂ D ⁺ , HDO, HDO#, PAH, PAH ⁻ , PAH ⁺ , PAH#, PAH-H, PAH-H ⁺ , PAH-H#, PAHD, PAH-D#, PAH-D ⁺	23
species	total	123

Notes. Closed-shell molecules are indicated in bold font, ices are indicated by a trailing #, and chemisorbed species are lead by a * sign. CH₂ is a reactive closed-shell species.

Appendix E: Transmission function

Part of the difference in the H₂ formation efficiency can be explained by the choice of different transmission function. Fig. E.1 shows the transmission function for α_{pc} using the Bell formulation or the transmission function in Cazaux & Tielens (2010). The Bell formulation gives a higher transmission in the quantum tunnelling part below 20 K while the exponential pre-factor in the Cazaux formulation is higher than the Bell pre-factor at high temperatures.

Appendix F: Tables of variable symbols

The main variable symbols are summarized in Table F.1 and F.2.

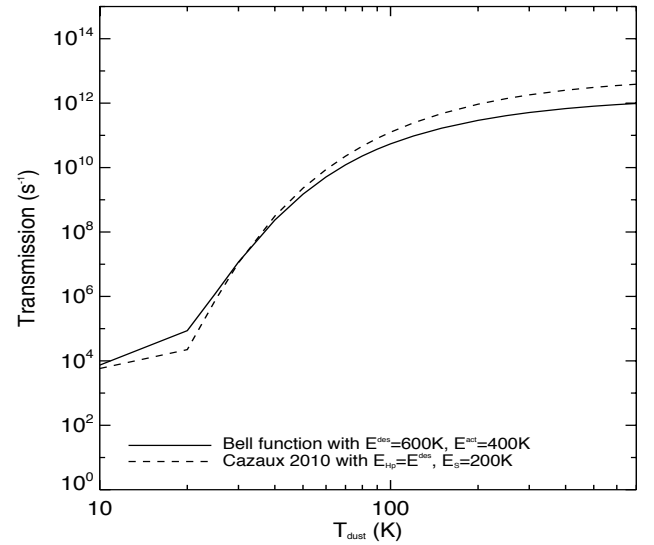


Fig. E.1. Transmission function α_{pc} using the Bell formulation or the formulation in Cazaux & Tielens (2010). The adopted values are given in the figure, the chosen value for the quantum width is 2.5 Å for silicate.

Table D.2. Main grain reactions involved in the formation and destruction of H₂ and HD. The energies are expressed in units of Kelvin.

Reaction				Comment		
1		H	→	H#		physisorption, barrierless
2		D	→	D#		–
3	H	+	*	→	*H#	$E_{\text{H}}^{\text{gc}} = E_{*}^{\text{act}} = (400) \text{ 900–15,900 K}$
4	H#	+	*	→	*H#	$E_{\text{H\#}}^{\text{pc}} = E_{*}^{\text{act}}$
5	D	+	*	→	*D#	$E_{\text{D}}^{\text{gc}} = E_{*}^{\text{act}} + \Delta E^{\text{H–D}}$
6	D#	+	*	→	*D#	$E_{\text{D\#}}^{\text{pc}} = E_{*}^{\text{act}} + \Delta E^{\text{H–D}}$
7		H#	→	H		$E_{\text{H\#}}^{\text{b}} = 600 \text{ K}$
8		D#	→	D		$E_{\text{D\#}}^{\text{b}} = E_{\text{H\#}}^{\text{b}} + \Delta E^{\text{H–D}}$
9	H#	+	$h\nu$	→	H	photodesorption
10	D#	+	$h\nu$	→	D	–
11	H#	+	CR	→	H	
12	D#	+	CR	→	D	
13			*H#	→	H	$E_{* \text{H\#}}^{\text{b}} = 10,000\text{–}25,000 \text{ K}$
14			*D#	→	D	$E_{* \text{D\#}}^{\text{b}} = E_{* \text{H\#}}^{\text{b}} + \Delta E^{\text{H–D}}$
15	*H#	+	$h\nu$	→	H	
16	*D#	+	$h\nu$	→	D	
17	*H#	+	CR	→	H	via CR induced UV
18	*D#	+	CR	→	D	–
19	H	+	H#	→	H ₂	Eley-Rideal (ER) mechanism, barrierless
20	D	+	H#	→	HD	–
21	H	+	D#	→	HD	–
22	H#	+	H#	→	H ₂	$E_{\text{H\#,H\#}}^{\text{act}} = 0\text{–}250 \text{ K}$ (Navarro-Ruiz et al. 2014)
23	H#	+	D#	→	HD	$E_{\text{H\#,D\#}}^{\text{act}} = E_{\text{H\#,H\#}}^{\text{act}} + \Delta E^{\text{H–D}} = 0\text{–}308 \text{ K}$
24	H	+	*H#	→	H ₂	ER mechanism, barrierless
25	H	+	*D#	→	HD	–
26	D	+	*H#	→	HD	–
27	H#	+	*H#	→	H ₂	$E_{* \text{H\#,H\#}}^{\text{act}} = E_{*}^{\text{act}}$
28	H#	+	*D#	→	HD	$E_{* \text{H\#,H\#}}^{\text{act}} = E_{*}^{\text{act}} + \Delta E^{\text{H–D}}$
29	D#	+	*H#	→	HD	$E_{* \text{H\#,D\#}}^{\text{act}} = E_{*}^{\text{act}} + \Delta E^{\text{H–D}}$
30	*H#	+	*H#	→	H ₂	$E_{* \text{H\#},* \text{H\#}}^{\text{act}} = 2 \times E_{*}^{\text{act}}$
31	*H#	+	*D#	→	HD	$E_{* \text{H\#},* \text{D\#}}^{\text{act}} = E_{* \text{H\#},* \text{H\#}}^{\text{act}} + \Delta E^{\text{H–D}}$
32	H ₂	+	*	→	*H#	$E_{\text{H}_2,*}^{\text{diss}} = 3481 \text{ K}$ (Diño et al. 2004)
33	HD	+	*	→	*D#	$E_{\text{HD},*}^{\text{diss}} = E_{\text{H}_2,*}^{\text{diss}} + \Delta E^{\text{H–D}}$, 1/2 of the total dissociation rate
34	HD	+	*	→	*H#	$E_{\text{HD},*}^{\text{diss}}$, 1/2 of the total dissociation rate

$\Delta E^{\text{H–D}} = 58 \text{ K}$ (5 meV), $\Delta E_{\text{PAH}}^{\text{CH–CD}} = 970 \text{ K}$ (83 meV), $\Delta E^{\text{H}_2\text{–HD}} = 415.8 \text{ K}$.

Table D.3. Main gas-phase and **singly-hydrogenated** PAH reactions. The energies are expressed in units of Kelvin.

			Reaction		Comment	
35			PAH	→ PAH#	physisorption	
36			PAH-H	→ PAH-H#	–	
37			PAH-D	→ PAH-D#	–	
38			PAH#	→ PAH	see eq. B.33	
39			PAH-H#	→ PAH-H	–	
40			PAH-D#	→ PAH-D	–	
41	PAH#	+	$h\nu$	→ PAH	photodesorption	
42	PAH-H#	+	$h\nu$	→ PAH-H	–	
43	PAH-D#	+	$h\nu$	→ PAH-D	–	
44	PAH#	+	CR	→ PAH	cosmic-ray induced photodesorption	
45	PAH-H#	+	CR	→ PAH-H	–	
46	PAH-D#	+	CR	→ PAH-D	–	
47	H	+	PAH	→ PAH-H	$E_{\text{PAH-H}_x, \text{H}}^{\text{act}} = 324 \text{ K}$ (Boschman et al. 2015)	
48	D	+	PAH	→ PAH-D	$E_{\text{PAH-H}_x, \text{D}}^{\text{act}} = E_{\text{PAH-H}_x, \text{H}}^{\text{act}} + \Delta E^{\text{H-D}}$, D-mass scaling of $1/\sqrt{2}$	
49			PAH-H	→ H	thermal H-detachment with $E_{\text{PAH-H}}^{\text{b}} = 16,250 \text{ K}$	
50			PAH-D	→ D	$E_{\text{PAH-D}}^{\text{b}} = E_{\text{PAH-H}}^{\text{b}} + \Delta E_{\text{PAH}}^{\text{CH-CD}}$	
51	PAH-H	+	$h\nu$	→ H	photodetachment, $E(\text{C-H}) = 1.4 \text{ eV}$ (16,250 K)	
52	PAH-D	+	$h\nu$	→ D	$E(\text{C-D}) = 4.367 \text{ eV}$ (50677.2 K)	
53	PAH-H	+	H	→ H ₂	$\sigma = 0.06 \text{ \AA}^2/\text{C atom}$, $E^{\text{act}} = 0 \text{ K}^a$	
54	PAH-H	+	D	→ HD	ten-fold H cross-section $\sigma = 0.06\text{--}0.6 \text{ \AA}^2/\text{C atom}$	
55	PAH-D	+	H	→ HD	same as for PAH-H	
56	H	+	PAH ⁺	→ PAH-H ⁺	$E_{\text{PAH-H}_x^+, \text{H}}^{\text{act}} = 116 \text{ K}$	
57	D	+	PAH ⁺	→ PAH-D ⁺	$E_{\text{PAH-H}_x^+, \text{D}}^{\text{act}} = E_{\text{PAH-H}_x^+, \text{H}}^{\text{act}} + \Delta E^{\text{H-D}}$	
58	PAH-H ⁺	+	e	→ PAH	dissociative recombination	
59	PAH-D ⁺	+	e	→ PAH	–	
60	PAH-H ⁺	+	H	→ PAH ⁺	Langevin rate (Montillaud et al. 2013)	
61	PAH-H ⁺	+	D	→ PAH ⁺	same as for PAH-H ⁺	
62	PAH-D ⁺	+	H	→ PAH ⁺	same as for PAH-H ⁺	
63	PAH-H ⁺	+	HD	→ PAH-D ⁺		
64	PAH-D ⁺	+	H ₂	→ PAH-H ⁺	endothermic, $\Delta E^{\text{reac}} = \Delta E^{\text{H}_2-\text{HD}} - \Delta E_{\text{PAH}}^{\text{CH-CD}}$	
65	H ₂	+	PAH	→ PAH-H	$E_{\text{H}_2, \text{PAH}}^{\text{diss}} - \text{H-H} = 3481 \text{ K}$	
66	HD	+	PAH	→ PAH-D	$E_{\text{HD, PAH}}^{\text{diss}} = E_{\text{H}_2, \text{PAH}}^{\text{diss}} + \Delta E^{\text{H}_2-\text{HD}}$	
67	PAH	+	$h\nu$	→ PAH ⁺	photoionisation	
68	PAH	+	e	→ PAH [−]	electron attachment	
69	PAH [−]	+	$h\nu$	→ PAH	photodetachment	
70	PAH ⁺	+	e	→ PAH	electron recombination	
71	PAH ⁺	+	X	→ PAH	charge exchange with species X	
72	PAH	+	X ⁺	→ PAH ⁺	X=H and C, rates from Wolfire et al. (2008)	
73	H	+	e [−]	→ H [−]	radiative attachment	
74	D	+	e [−]	→ D [−]	radiative attachment	
75	H	+	H [−]	→ H ₂	associative detachment	
76	H	+	D [−]	→ HD	associative detachment	
77	D	+	H [−]	→ HD	associative detachment	
78	H	+	D	→ HD	radiative association (Stancil & Dalgarno 1997)	
79	H ₂	+	D ⁺	→ HD	Honvault & Scribano (2013)	
80	HD	+	H ⁺	→ H ₂	$\Delta E^{\text{reac}} = -416 \text{ K}$	
81	H ₂	+	D	→ HD	Simbotin et al. (2011)	
82	HD	+	H	→ H ₂	$\Delta E = -416 \text{ K}$	
83	H + H	+	H	→ H ₂	three-body reactions	
84	H + H	+	H ₂	→ H ₂	–	
85	H ₂	+	$h\nu$	→ H	photodissociation including self-shielding	
86	HD	+	$h\nu$	→ H	photodissociation including self-shielding	
87	H ₂	+	CR	→ H	by secondary electrons and CR-generated UV photons	
88	HD	+	CR	→ D	–	

^a Mennella et al. (2012); Rauls & Hornekar (2008). $\Delta E^{\text{H-D}} = 58 \text{ K}$ (5 meV), $\Delta E_{\text{PAH}}^{\text{CH-CD}} = 970 \text{ K}$ (83 meV), $\Delta E^{\text{H}_2-\text{HD}} = 415.8 \text{ K}$.

Table F.1. Variables used in the manuscript.

Variable	Symbol	Units & remarks
Species i mass	m_i	grams
Dust grain radius squared	r^2	cm^2 , input parameter
Dust number density	n_d	cm^{-3}
Number density of gas-phase species i	n_i	cm^{-3}
Surface density of adsorption sites	N_{surf}	$1.5 \times 10^{15} \text{ cm}^{-2}$, input parameter
Number of adsorption sites per ice monolayer	nb_{site}	no units, $nb_{\text{site}} = 4\pi N_{\text{surf}} r^2$
Surface site cross-section	$\sigma_{\text{surf,site}}$	$\sigma_{\text{surf,site}} = 1/N_{\text{surf}} \text{ cm}^2$
Total number density of chemisorption sites	$n_{\text{surf,chem}}$	$n_{\text{surf,chem}} = nb_{\text{site}} n_d = 4\pi N_{\text{surf}} r^2 n_d \text{ cm}^{-3}$
Number density of physisorbed species i	$n_{\#,i}$	cm^{-3}
Number density of chemisorbed species i	$n_{*,i}$	cm^{-3}
Number density of unoccupied chemisorption sites	n_*	$n_* = n_{\text{surf,chem}} - \sum_i n_{*,i} \text{ cm}^{-3}$
Number density of chemically active physisorbed species i	n_i^{act}	cm^{-3}
Number of chemically active physisorption layers	N_{act}	no units, an input parameter with typical value 1–10
Total number of density of physisorbed species (ice)	$n_{\#, \text{tot}}$	$n_{\#, \text{tot}} = \sum_i n_{\#,i} \text{ cm}^{-3}$
Number of physisorbed ice layers per grain	N_{layer}	no units, $N_{\text{layer}} = n_{\#, \text{tot}} / (n_d nb_{\text{site}})$
Fraction of available adsorption sites	f_{avail}	1 for physisorption for chemisorption = $n_*/n_{\text{surf,chem}}$ if $N_{\text{layer}} < 1$, = 0 if $N_{\text{layer}} \geq 1$
Gas temperature	T_g	K
Dust temperature	T_d	K
General activation barrier width	a_{λ}	\AA
Activation barrier	E_{act}	K
Species mass in atomic mass units	m_{amu}	amu
General adsorption rate	R_i^{ads}	s^{-1}
General sticking coefficient	S_i	no units, between 0 and 1
General Bell's formula	Q_{Bell}	no units
Physisorption rate	R_i^{EP}	s^{-1}
Physisorption sticking coefficient	S_{phys}	no units, between 0 and 1
Species i thermal speed	v_i^{th}	cm s^{-1}
Chemisorption activation energy	E_i^{gc}	ergs
Chemisorption rate	R_i^{gc}	s^{-1}
Chemisorption Bell's function	Q_i^{gc}	no units
Chemisorption sticking coefficient	S_{chem}	no units, between 0 and 1
Chemisorption activation barrier width	a_i^{gc}	cm, assuming a rectangular-shaped barrier
Desorption energy	E_i^{des}	ergs
Binding energy	E_i^{b}	ergs, physisorption and chemisorption
Desorption activation energy	$E_i^{\text{des,act}}$	ergs, non-null for desorption from chemisorption sites
Surface vibration frequency	$\nu_{0,i}$	$\nu_{0,i} = \sqrt{(2N_{\text{surf}} E_i^{\text{b}})/(\pi^2 m_i)} \text{ Hz}$
Activation barrier for desorption	$E_i^{\text{des,act}}$	ergs, non null for chemisorption
Desorption energy	E_i^{des}	ergs, for either the physisorbed ($=E_i^{\text{b}}$) chemisorbed ($=E_i^{\text{b}} + E_i^{\text{des,act}}$)
Total desorption rate from a physisorption site	$R_i^{\text{des,pg}}$	s^{-1}
Thermal desorption rate from a physisorption site	$R_i^{\text{pg,th}}$	s^{-1}
Photodesorption rate from a physisorption site	$R_i^{\text{pg,ph}}$	s^{-1}
Photodesorption yield	Y_i	no units
UV flux enhancement w.r.t. to the ISM value	χF_{Draine}	$1 \chi F_{\text{Draine}} = 1.9921 \times 10^8 \text{ photons/cm}^2/\text{s}$
Cosmic-Ray induced desorption rate from a physisorption site	$R_i^{\text{pg,CR}}$	s^{-1}
Activation barrier width for desorption from a chemisorption site	$a_i^{\text{des,act}}$	cm
Total desorption rate from a chemisorption site	$R_i^{\text{des,cg}}$	s^{-1}
Thermal desorption from a chemisorption site	$R_i^{\text{cg,th}}$	s^{-1}
Photodesorption rate from a chemisorption site	$R_i^{\text{cg,ph}}$	s^{-1}
Cosmic-ray induced desorption from a chemisorption site	$R_i^{\text{cg,CR}}$	$\simeq 0 \text{ s}^{-1}$
Fraction of time a grain remains at 70 K up upon a cosmic-ray hit	$f(70K)$	no units
Thermal desorption rate for a dust grain at 70 K	$R_i^{\text{pg,th}}(70K)$	s^{-1}
Thermal diffusion rate for a dust grain at 70 K	$R_i^{\text{diff,th}}(70K)$	s^{-1}
Thermal surface diffusion rate	$R_i^{\text{diff,th}}$	s^{-1} , includes quantum tunnelling effect
Cosmic-Ray induced surface diffusion rate	$R_i^{\text{diff,CR}}$	s^{-1}
Bell's formula for the diffusion processes	Q_i^{diff}	no units
Diffusion activate energy	E_i^{diff}	ergs
Diffusion activation barrier width	a_i^{diff}	cm
Total surface diffusion rate	R_i^{diff}	$R_i^{\text{diff}} = R_i^{\text{diff,th}} + R_i^{\text{diff,CR}} \text{ s}^{-1}$, $P_i^{\text{diff}} = R_i^{\text{diff}}/\nu_{0,i}$
Activation barrier width for diffusion	a_i^{diff}	cm

Notes. The index i means that the variable applies to species i . Depending on the process, the species i is a gas-phase, physisorbed, or chemisorbed species.

Table F.2. Variables used in the manuscript, part 2.

Variable	Symbol	Units & remarks
Hydrogen diffusion barrier between physisorption sites	$E_{H\#}^{\text{diff}}$	ergs
Hydrogen diffusion barrier between chemisorption sites	$E_{*H\#}^{\text{diff}}$	ergs
Deuterium diffusion barrier between physisorption sites	$E_{D\#}^{\text{diff}}$	ergs
Deuterium diffusion barrier between chemisorption sites	$E_{*D\#}^{\text{diff}}$	ergs
Physisorbed hydrogen desorption energy	E_p^{des}	ergs
Physisorbed deuterium desorption energy	E_{Dp}^{des}	ergs
Chemisorbed hydrogen desorption energy	E_c^{des}	ergs
Chemisorbed deuterium desorption energy	E_c^{des}	ergs
Surface reaction rate coefficient between species i and j	k_{ij}	$\text{cm}^3 \text{s}^{-1}$
Surface reaction probability	κ_{ij}	no units, between 0 and 1
Surface reaction activation barrier	E_i^{act}	ergs
Surface reaction activation barrier width	a_{ij}^{pg}	cm
Hydrogen thermal desorption rate from a physisorption site	$R_{H\#}^{\text{pg}}$	s^{-1}
Hydrogen diffusion rate between physisorption sites	$R_{H\#}^{\text{diff}}$	s^{-1}
Hydrogen transfer rate from a physisorption to a chemisorption site	$R_{H\#}^{\text{pc}}$	s^{-1}
Acatavation barrier energy for H transfer from a physisorption to a chemisorption site	$E_{H\#}^{\text{act}}$	ergs
Bell's function for H transfer from a physisorption to a chemisorption site	$Q_{H\#}^{\text{pc}}$	no units
Hydrogen transfer rate from a chemisorption to a physisorption site	$R_{H\#}^{\text{cp}}$	s^{-1}
Eley-Rideal H_2 formation rate (physisorption site)	$R_{H_2}^{\text{ep}}$	s^{-1}
Eley-Rideal H_2 formation rate (chemisorption site)	$R_{H_2}^{\text{ec}}$	s^{-1}
H_2 formation rate after encounter between a physisorbed and a chemisorption H-atom	$R_{H\#, *H\#}$	$\text{cm}^3 \text{s}^{-1}$
Analytical H_2 formation rate	$R_{H_2}^{\text{Cazaux}}$	s^{-1}
PAH effective radius	a_{PAH}	cm
PAH number of carbon atoms	N_C	no units
PAH number of hydrogen atoms	N_H	no units
PAH ionization potential	IP_{PAH}	ergs
Hydrogenated PAH hydrogen association rate coefficient	$k_{\text{PAH}-\text{H}_x, \text{H}}$	$\text{cm}^3 \text{s}^{-1}$
Hydrogen association on PAH- H_x activation energy	$E_{\text{PAH}-\text{H}_x, \text{H}}^{\text{act}}$	ergs
Hydrogenated PAH hydrogen abstraction rate coefficient	$k_{\text{PAH}-\text{H}_x}$	$\text{cm}^3 \text{s}^{-1}$
Effective temperature upon absorption of a photon of energy $h\nu$	T_e	K
PAH internal temperature	T_{PAH}	K
Unimolecular PAH thermal dissociation rate at T_e	$R_{\text{PAH}-\text{H}_x, T_e}$	s^{-1}
Hydrogen binding energy on PAH- H_x	E_0	ergs, $\sim 1\text{--}2 \text{ eV}$
Yield for PAH- H_x photodissociation	$Y_{\text{PAH}-\text{H}_x, \text{UV}}$	no units, $=0$ for $h\nu < E_0$
Typical PAH IR photon emission rate	R_{IR}	$\sim 1 \text{ s}^{-1}$
Thermal unimolecular dissociation rate	$R_{\text{PAH}-\text{H}_x, \text{therm}}$	s^{-1}
Hydrogen association rate coefficient for (hydrogenated) PAHs cations	$k_{\text{PAH}-\text{H}_x^{n+}, \text{H}}$	$\text{cm}^3 \text{s}^{-1}$
Activation energy for hydrogen association for PAH cations	$E_{\text{PAH}-\text{H}_x^{n+}, \text{H}}^{\text{act}}$	ergs
Hydrogenated ionized PAH hydrogen abstraction rate coefficient	$k_{(\text{PAH}-\text{H}_x)^{n+}}$	$\text{cm}^3 \text{s}^{-1}$
Energetic particle induced photoionisation rate coefficient	$k_{\text{pi}, \text{MeV}}$	$\text{cm}^3 \text{s}^{-1}$
Energetic particle induced photodetachment rate coefficient	$k_{\text{pd}, \text{CR}}$	$\text{cm}^3 \text{s}^{-1}$
Singly-ionized PAH cations electron recombination rate coefficient	k_{er}	$\text{cm}^3 \text{s}^{-1}$
Multiply-ionized PAH cations electron recombination rate coefficient	k'_{er}	$\text{cm}^3 \text{s}^{-1}$
PAH shape correction factor	ϕ_{PAH}	$\phi_{\text{PAH}} = \sigma_{\text{disk}}/\sigma_{\text{sphere}}$
PAH electron attachment rate coefficient	k_{ea}	$\text{cm}^3 \text{s}^{-1}$
Electron sticking coefficient on PAHs	$S_{\text{PAH}}(e^-)$	no units
Mutual neutralisation rate coefficient	k_{mn}	$\text{cm}^3 \text{s}^{-1}$
Electron collisional detachment rate coefficient	k_{nd}	$\text{cm}^3 \text{s}^{-1}$
Neutral PAH charge-exchange reactions	$k_{\text{ce}, 0}$	$\text{cm}^3 \text{s}^{-1}$
Charged PAH charge-exchange reactions	$k_{\text{ce}, n}$	$\text{cm}^3 \text{s}^{-1}$
Double charge transfer reaction	k_{di}	$\text{cm}^3 \text{s}^{-1}$
PAH adsorption/desorption energy	$E_{\text{PAH}, \text{des}}$	$\text{cm}^3 \text{s}^{-1}$
Total H_2 formation rate according to Cazaux & Tielens (2002, 2004)	$R_{\text{H}_2}^{\text{Cazaux}}$	s^{-1}
H_2 recombination efficiency	ϵ	Cazaux & Tielens (2002)
Total H_2 formation rate according to Jura (1974, 1975a,b)	$R_{\text{H}_2}^{\text{Jura}}$	s^{-1}

Notes. See notes for Table F.1.